* Entropy change during a chemical reaction.
    — Exothermic reactions.

$$\Delta S^{\ominus}_{Total} = \Delta S^{\ominus}_{system} + \Delta S^{\ominus}_{surrounding}.$$

ΔS_{Total} is positive and the reaction is likely to occur.

— Endothermic reactions: ΔS_{Total} is negative and is most unlikely ~~not~~ to occur.

* $$\Delta S^{\ominus}_{system} = \Delta S^{\ominus}_{products} - S^{\ominus}_{reactants}.$$
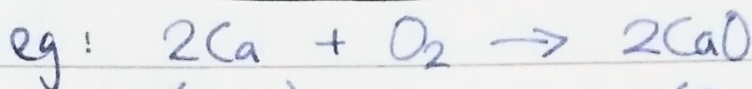
eg: $2Ca + O_2 \longrightarrow 2CaO$
      $2(4140) + 205 \longrightarrow 2(39.7)$
      $\therefore \Delta S^{\ominus}_{system} = -208.4 \ JK^{-1} mol^{-1}$

The negative $\Delta S^{\ominus}_{system}$ shows that the disorderness has decreased.

* $$\Delta S^{\ominus}_{surrounding} = \frac{-\Delta H^{\ominus}_{reaction}}{T}$$

$\Delta S^{\ominus}_{surrounding}$: $-ve$ for endo
                 $+ve$ for exo.

eg: $2Ca + O_2 \rightarrow CaO$
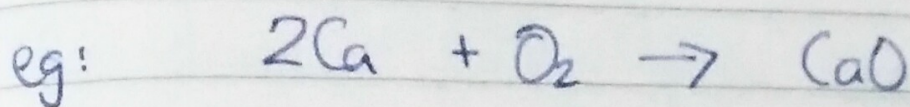
$$\Delta S^{\ominus}_{surrounding} = \frac{-(-1270200)}{298}$$

$$= +4262.4 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta S^{\ominus}_{total} = -208.4 + 4262.4$$
$$= +4054 \text{ JK}^{-1}\text{mol}^{-1}$$

* <u>Feasibility</u>:

	Exo	Endo
$\Delta S^{\ominus}_{total}$:	+ve	-ve.
$\Delta H^{\ominus}_{reaction}$:	-ve	+ve

To check thermodynamic feasibility, for a reaction, ΔH is not enough; ΔS_{total} has to be checked.

18/8/15.

* <u>Gibbs Free Energy.</u>

$$\Delta S_{total} = \Delta S_{sys} - \frac{\Delta H_{Reaction}}{T}$$

$$-T\Delta S_{total} = -T\Delta S_{sys} + \Delta H_{Reaction}$$

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

or

$$\Delta G = -T\Delta S_{sys} + \Delta H_{reaction}$$

ΔG : change in Gibbs free energy.

$\Delta G = -ve$ for feasible reaction.

* <u>Gibbs free energy of formation:</u> The free energy change when 1 mole of a compound is formed from its elements in their **s**tandard state.

$$G = H - TS_{sys}$$
$$\Delta G = \Delta H - T\Delta S_{sys}$$

* The <u>standard Gibbs frees energy change</u> of a reaction is the free energy change when the amount of reactant shown in the stoichiometric equation reacts under standard conditions to give the products.
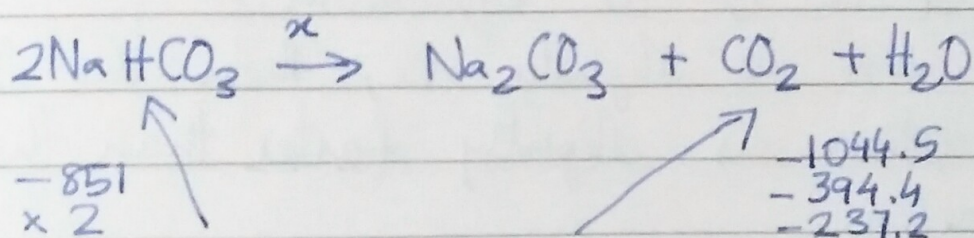
eg: $2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$
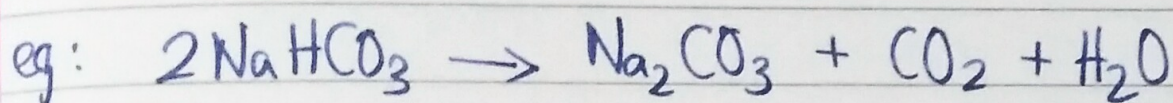
$NaHCO_3 \; \Delta G_{(f)} = -851 \text{ kJ mol}^{-1}$
$Na_2CO_3 \; \Delta G_f \;\; = -1044.5 \text{kJ mol}^{-1}$
$CO_2 \;\; \Delta G_f = -394.4 \text{ kJ mol}^{-1}$
$H_2O \;\;\; \Delta G_f \;\; = -237.2 \text{ kJ mol}^{-1}$

$2NaHCO_3 \xrightarrow{x} Na_2CO_3 + CO_2 + H_2O$

-851
$\times 2$

-1044.5
-394.4
-237.2

$2Na + H_2 + 2C + 3O_2$
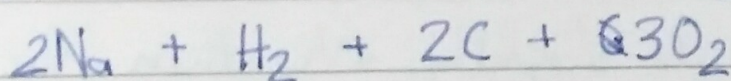
$x = 1702 - 1044.5 - 394.4 - 237.2$
$\;\; = +25.9 \text{ kJ mol}^{-1}$

* Equilibrium Reactions.

```
         |              Equilibrium
         |                  ↓
         |                 /\
 Entropy |                /  \
         |              /      \
         |            /          \
         |          /
         |_____/_____
                     Time
```
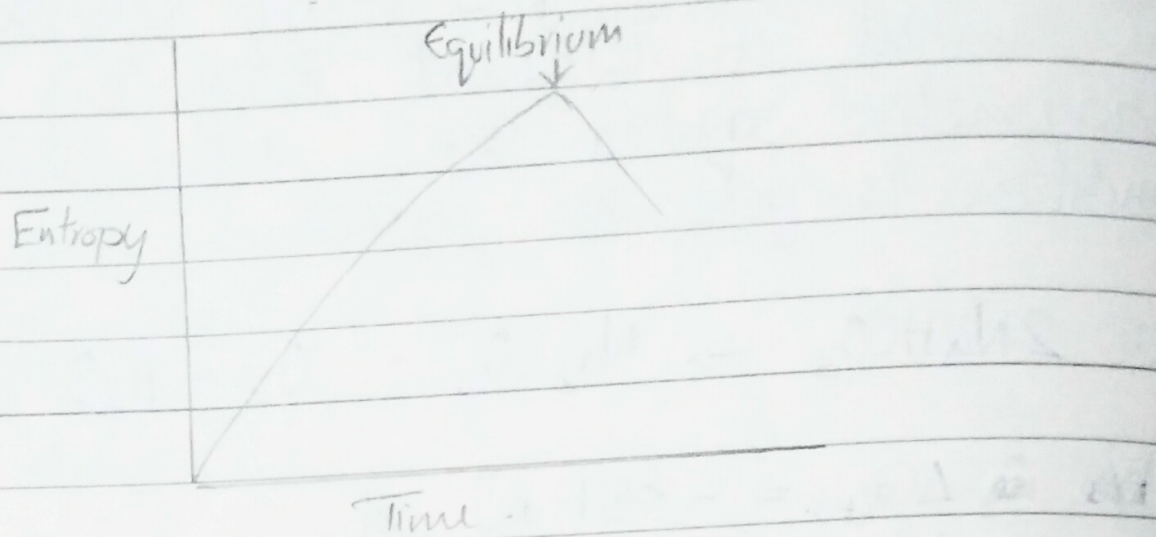
→ Disorderness is maximum at equilibrium. so is entropy.

→ ΔG is 0 at equilibrium.

→ If ΔG is slightly $-ve$, then the forward reaction is slightly faster than the backward reaction.

→ If ΔG is slightly $+ve$, then the backward reaction is slightly faster than the forward reaction.

→ If ΔG is highly $-ve$, then the reaction is irreversible and is nearing completion.

* <u>Energy to do work.</u>

$$\Delta H = \Delta G + T\Delta S_{sys}$$

Total
energy
(↓ under ΔH)

Energy available
to do work
(↓ under ΔG)

↳ Energy not available
to do work (wasted)
(under $T\Delta S_{sys}$)