

This small peak is because we assumed most of A converted to C  
 NOT all of it, therefore some B can be in proximity of the electrode

\* For each electroactive reaction, you expect two peaks:

one for oxidation and one for reduction

We said that the potential of a reversible reaction is the mean of  $E_{p,c}$  and  $E_{p,a}$  (Potentials at peak Cathodic/Anodic current)

Therefore, two peaks should kinda be symmetric around  $0.5 \text{ V}$  for the 1<sup>st</sup> reaction ( $A + e \rightleftharpoons B$ ) and  $1.0 \text{ V}$  for the 2<sup>nd</sup> reaction ( $C + e \rightleftharpoons D$ )

\* At  $0.05 \frac{\text{mV}}{\text{s}}$ , it would take  $4 \text{ s}$  to scan from  $0.4 \rightarrow 0.6$

This is based on the assumption that most of the electrochemical reaction takes place at  $\pm 100 \text{ mV}$  around its  $E^\circ$ .

$$\frac{0.6 - 0.4}{0.05} = 4 \text{ s} \Rightarrow \frac{4 \text{ s}}{100 \text{ ms}} = 40 \times \text{half life of B}$$

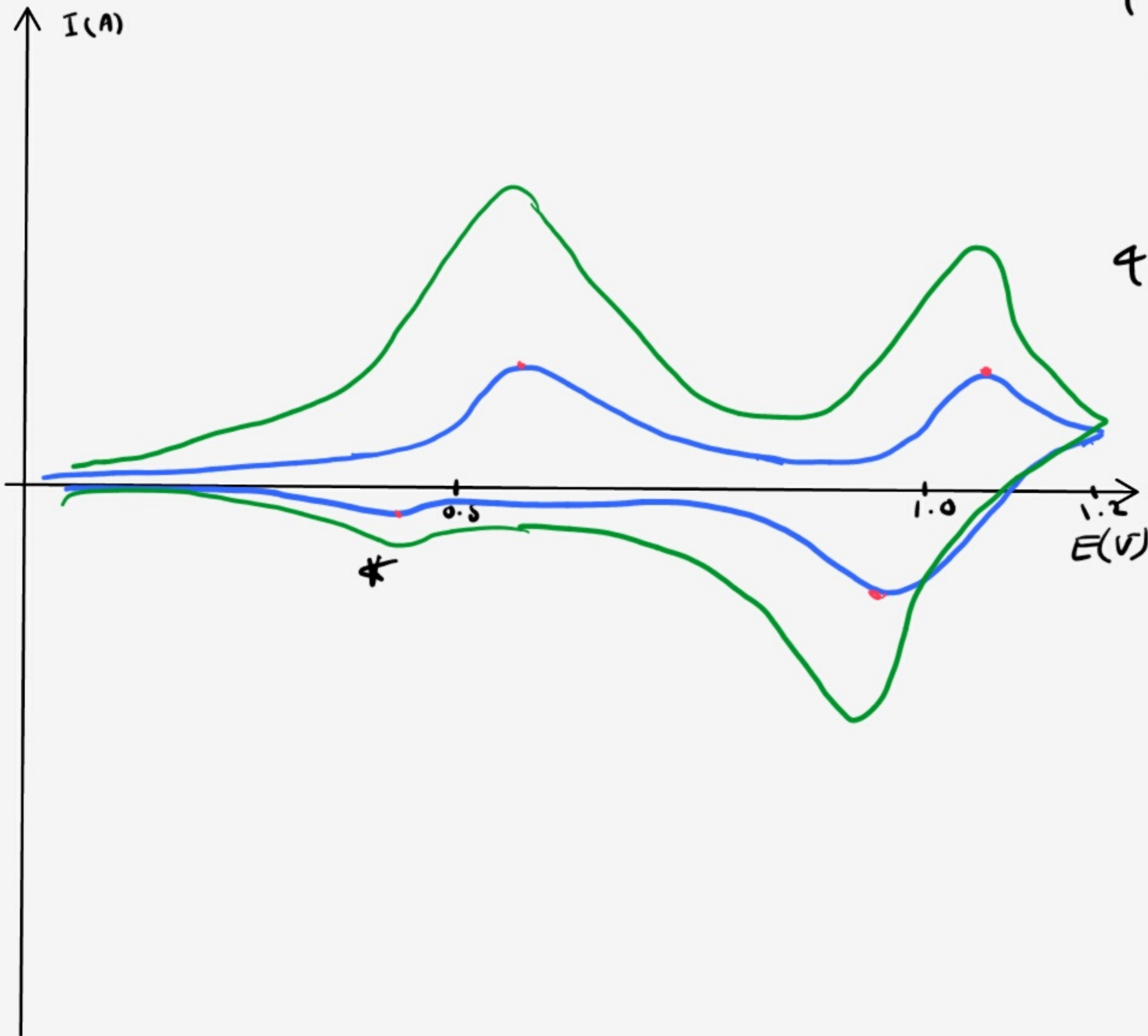
It is safe to say all of A converts to C

$\Rightarrow I_{p,a,1}, I_{p,a,2}$  are of the same magnitude

\* We also expect to have a cathodic peak for rxn 2,

because it is reversible! However, the intermediate rxn ( $B \rightarrow C$ ) does not allow the formation of B as it only converts B to C, NOT the reverse rxn.

Converts B to C, NOT the reverse rxn.



↑ Peak current increases  
as we increase the sweep rate.  
(Not to scale)

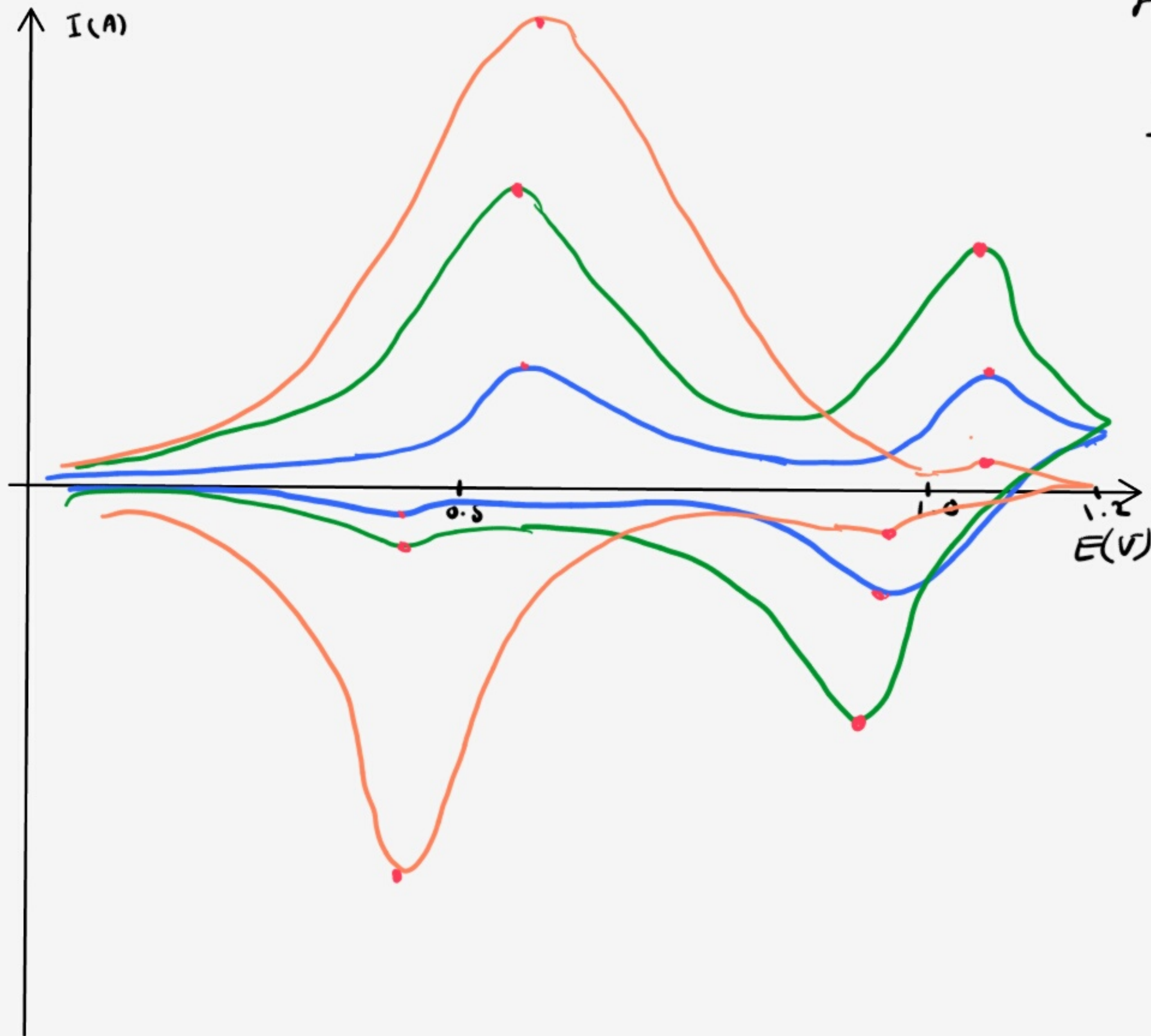
↑ at  $1 \text{ V/s}$

$$\frac{0.6 - 0.4}{1} = 0.2 \text{ s}$$

$$\frac{0.2 \text{ s}}{100 \text{ ms}} = 2 \times \text{half life } \underline{B}$$

⇒ a bigger peak is expected  
at \* (wrt  $0.05 \text{ V/s}$ )





At  $20 \text{ V/s}$ ,

$$\frac{0.6 - 0.4}{20} \approx 0.01 \text{ s}$$

$\Rightarrow$  which is less than half-life of B!

$\Rightarrow$  2<sup>nd</sup> reaction doesn't proceed, but small peaks are observed due to slight conversion of  $B \rightarrow C$