Assignments

1. Peroxodisulfate ions react with iodide ions according to the reaction $S_2O_8^{2-}(aq) + 2\ I^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_2(aq)$

For that reaction, the reaction rate at the start of the reaction was determined at constant temperature but different initial concentrations of the reactants.

The table below shows you the different measurement results.

	$[I^-]_0$ (mol.L^{-1})	$[S_2O_8^{2-}]_0$ (mol.L^{-1})	v_0 (mol.L^{-1}.s^{-1})
1	0.040	0.020	3.2 x 10^{-6}
2	0.030	0.030	3.6 x 10^{-6}
3	0.010	0.020	0.80 x 10^{-6}
4	0.040	0.040	6.4 x 10^{-6}
5	0.080	0.020	6.4 x 10^{-6}

Which rate equation and which value of the reaction rate constant do you derive from this?

	equation rate	*k*
<A>	$v = k\ .[I^-]^2.\ [S_2O_8^{2-}]$	0.10 mol.L^{-1}.s^{-1}
<B>	$v = k\ .[I^-]^2.\ [S_2O_8^{2-}]$	0.10 L^2.mol^{-2}.s^{-1}
<C>	$v = k\ .[I^-]\ .\ [S_2O_8^{2-}]$	4.0.10^{-3} mol.L^{-1}.s^{-1}
<D>	$v = k\ .[I^-]\ .\ [S_2O_8^{2-}]$	4.0.10^{-3} L.mol^{-1}.s^{-1}

<u>**Answer**</u>
(took **8 minutes to solve** in rough)
(took **18 minutes to write explanation** below)

Given Data

The given equation is **$S2O_8^{2-}$(aq) + 2 I^-(aq) → 2 SO_4^{2-}(aq) + I2 (aq)**

Experimental Data

	$[I^-]0$ (mol.L^{-1})	$[S2O_8^{2-}]0$ (mol.L^{-1})	*v*0 (mol.L^{-1}.s^{-1})
1	0.040	0.020	3.2×10^{-6}
2	0.030	0.030	3.6×10^{-6}
3	0.010	0.020	0.80×10^{-6}
4	0.040	0.040	6.4×10^{-6}
5	0.080	0.020	6.4×10^{-6}

We have to find the **rate equation & rate constant**

Possible answers are

	equation rate	*k*
<A>	$v = k\,.[I^-]^2.\,[S2O_8^{2-}]$	0.10 mol.L^{-1}.s^{-1}
<B>	$v = k\,.[I^-]^2.\,[S_2O_8^{2-}]$	0.10 L^2.mol^{-2}.s^{-1}
<C>	$v = k\,.[I^-]\,.\,[S2O_8^{2-}]$	4.0.10^{-3} mol.L^{-1}.s^{-1}
<D>	$v = k\,.[I^-]\,.\,[S2O_8^{2-}]$	4.0.10^{-3} L.mol^{-1}.s^{-1}

Formulas to be used

i) Let **m & n** be the order of the reaction for the reactants **I^- & $S2O_8^{2-}$** respectively

Thus, the general rate equation is

$v = k\,[I^-]^m\,.\,[S2O_8^{2-}]^n$

Primary Focus

In order to find the rate equation (the solution of this question) we need to

determine the values of m & n

Solution

First, observe the experimental data carefully

	$[I^-]0$ (mol.L^{-1})	$[S2O_8^{2-}]0$ (mol.L^{-1})	*v*0 (mol.L^{-1}.s^{-1})
1	0.040	0.020	3.2×10^{-6}
4	0.040	0.040	6.4×10^{-6}
5	0.080	0.020	6.4×10^{-6}

In 1 & 4 the Molar concentration of **I^- is constant**
In 1 & 5 the Molar concentration of **$S2O_8^{2-}$ is constant**

(***Tip:*** *For questions that ask to determine rate equation from experimental data;* ***always take the equal values of molar concentration****!)*

Applying rate law to 1 & 4

$(v0)1 = k\ ([I^-]1)^m\ .\ ([S2O_8^{2-}]1)^n$ …(i)

$(v0)4 = k\ ([I^-]4)^m\ .\ ([S2O_8^{2-}]4)^n$ …(ii)

Divide (i) with (ii)

We get

$$\frac{(v0)1 = k\ ([I^-]1)^m\ .\ ([S2O_8^{2-}]1)^n}{(v0)4 = k\ ([I^-]4)^m\ .\ ([S2O_8^{2-}]4)^n}$$

Substituting the values

$$\frac{3.2 \times 10^{-6}}{6.4 \times 10^{-6}} = \frac{k\ (0.040)^m\ .\ (0.020)^n}{k\ (0.040)^m\ .\ (0.040)^n}$$

Simplifying

$$\frac{1}{2} = \left[\frac{0.020}{0.040}\right]^n$$

Simplifying

$$\frac{1}{\ } = \left[\frac{1}{\ }\right]^n$$

2 2

Therefore n = 1

Similarly,

Applying rate law to 1 & 5

$(v0)1 = k ([I^-]1)^m . ([S2O_8^{2-}]1)^n$ ...(i)

$(v0)4 = k ([I^-]5)^m . ([S2O_8^{2-}]5)^n$ ...(ii)

Divide (i) with (ii)

We get

$$\frac{(v0)1 = k ([I^-]1)^m . ([S2O_8^{2-}]1)^n}{(v0)4 = k ([I^-]5)^m . ([S2O_8^{2-}]5)^n}$$

Substituting the values

$$\frac{3.2 \times 10^{-6}}{6.4 \times 10^{-6}} = \frac{k (0.040)^m . (0.020)^n}{k (0.080)^m . (0.020)^n}$$

Simplifying

$$\frac{1}{2} = [\frac{0.040}{0.080}]^m$$

Simplifying

$$\frac{1}{2} = [\frac{1}{2}]^m$$

Therefore m = 1

Thus m = 1 & n =1

Substituting these values in rate law eqn: $v = k [I^-]^m . [S2O_8^{2-}]^n$

We get: $\mathbf{v = k [I^-] . [S2O_8^{2-}]}$

Now, **To calculate k**

$$k = \frac{v}{[I^-] \,.\, [S2O_8^{2-}]}$$

Substituting the values & taking dimensions

$$k = \frac{3.2 \times 10^{-6}}{(0.040) \times (0.020)} \quad \frac{[mol]\,[L]\,[L]}{[mol]\,.\,[mol]\,[L]\,[s]}$$

Simplifying

k = 0.004 $L.mol^{-1}.s^{-1}$ or **4.0 x 10^{-3} $L.mol^{-1}.s^{-1}$** & **$v = k\,[I^-]\,.\,[S2O_8^{2-}]$**

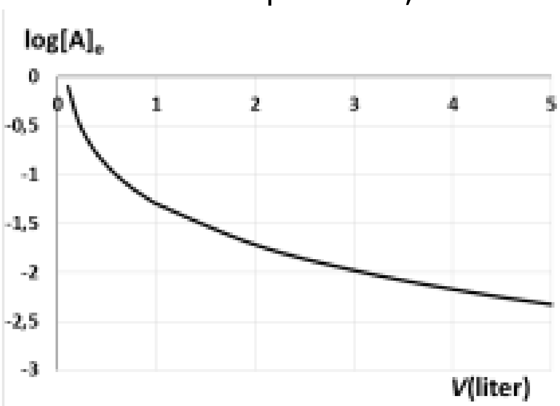
Thus, the correct option is **D**

<D>	***v* = *k* .$[I^-]\,.\,[S2O_8^{2-}]$**	4.0.10^{-3} **$L.mol^{-1}.s^{-1}$**

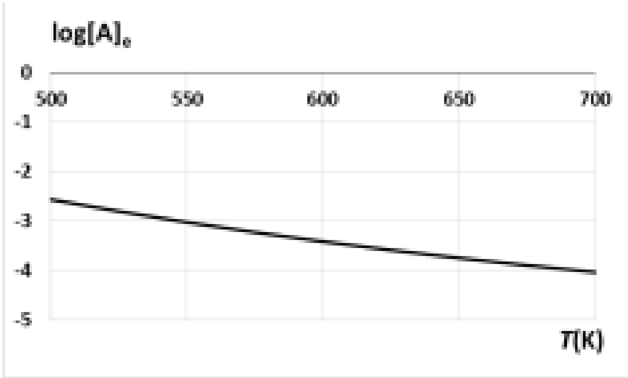
*(Tip: We do not need to calculate k since **the unit itself tells us the correct option)***

2. The (logarithm of the) equilibrium concentration of substance A is shown in the graphs below:

a) as a function of the volume of the reaction vessel at constant temperature;



b) as a function of the temperature at constant volume of the reaction vessel.



What equilibrium reaction do these two graphs correspond to?

<A> A (g) + heat ⇌ B (g) + C (g)
<B> A (g) ⇌ B (g) + C (g) + heat
<C> A (g) + B (g) + heat ⇌ C (g)
<D> A (g) + B (g) ⇌ C (g) + heat

Answer
(Took 7 minutes to solve)
(Took 12 minutes to write solution)

To Find
For this question, we have to determine which of the following reactions (given in the options) represent the two graphs above.

Major Focus

i) Analyse the $\log[A]_e$ versus Volume graph & **determine if reactant(s) is/are greater/less than product(s)**

ii) Analyse the $\log[A]_e$ versus Temperature graph & **determine if the equilibrium reaction is endothermic or exothermic**

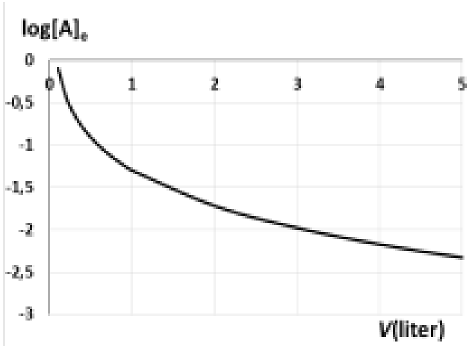
Solution

First off consider that,
Log of the reactant concentration A ∝ Molar concentration of A

Or

Log $[A]_e$ ∝ [A]

Keeping this in mind, let's analyse the first graph



As can be seen, Log $[A]_e \propto \frac{1}{V}$

Or in simpler terms, as Log of concentration A **decreases** Volume of the vessel **increases**

Thus, As the **concentration of A <u>decreases,</u> vessel volume <u>increases</u>**

Which means as the reaction takes place (reactant A decreases) the volume **should increase as a result of product formation**
Thus **No. of Reactants < No. of Products**

Now let's analyse the options given to us

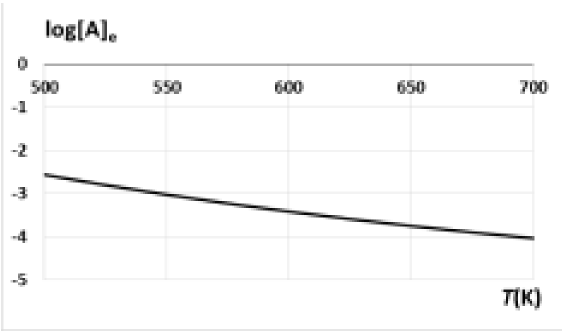
<A> A $_{(g)}$ + heat ⇌ B $_{(g)}$ + C $_{(g)}$
<B> A $_{(g)}$ ⇌ B $_{(g)}$ + C $_{(g)}$ + heat
<C> A $_{(g)}$ + B $_{(g)}$ + heat ⇌ C $_{(g)}$
<D> A $_{(g)}$ + B $_{(g)}$ ⇌ C $_{(g)}$ + heat

Options **A and B have higher no. of products** than C and D

Thus, **the correct answer is either A or B**

<A> A $_{(g)}$ + heat ⇌ **B $_{(g)}$ + C $_{(g)}$**
<B> A $_{(g)}$ ⇌ **B $_{(g)}$ + C $_{(g)}$** + heat

To further determine the exact answer, let us analyse the second graph



As can be seen,

$$\text{Log } [A]_e \propto \frac{1}{T}$$

Since $\text{Log } [A]_e \propto [A]$

Therefore $[A] \propto \frac{1}{T}$

Thus, as the reaction takes place, reactant A reduces and **temperature increases**

In other words, **this reaction should be exothermic** or produces heat

From the two options we shortlisted

<A> $A_{(g)}$ + **heat** $\rightleftharpoons$ $B_{(g)} + C_{(g)}$

<B> $A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$ + **heat**

Only B, evolves heat, or **is exothermic**

Therefore, the answer to our question is B

<B> $A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$ + heat