## TOPIC 11 ANSWERS TO EXERCISES

## Topic 11 Exercise 1

1. change in concentration of reactants or products per unit time
2. a) $1 \operatorname{wrt} \mathrm{~A}, 2 \operatorname{wrt} \mathrm{~B}$
b) 3
c) $\quad 250 \mathrm{~mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$
d) $\quad 2.5 \times 10^{-4} \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
3. $\quad 8.3 \times 10^{-3} \mathrm{~mol}^{-1} \mathrm{dm}^{3} \mathrm{~s}^{-1}$
rate determining step does not involve hydrogen
4. $\quad$ rate $=\mathrm{k}\left[\mathrm{PCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]^{2} \quad \mathrm{k}=1.05 \times 10^{-3} \mathrm{~mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$
5. $\quad 2.00 \mathrm{~mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$
6. $\quad$ rate $=k\left[\mathrm{H}_{2}\right][\mathrm{NO}]^{2} \quad \mathrm{k}=8.3 \times 10^{4} \mathrm{~mol}^{-2} \mathrm{dm}^{6} \mathrm{~s}^{-1}$

Topic 11 Exercise 2
1.

a) gradient of tangent at $t^{\prime}=0=(0.50-0.3475) / 1000=1.5 \times 10^{-4} \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
b) gradient of tangêt at $\mathrm{t}=1000=(0.37-0.315) / 500=1.1 \times 10^{-4} \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
c) gradient of tangent at $t=2500=(0.2925-0.17) / 2000=6.1 \times 10^{-5} \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
d) As the reaction progresses the concentration of reactants decreases, so the collision frequency decreases and the reaction slows down
e) gradient of tangent at $\left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right]=0.25=(0.265-0.195) / 1000$ $=7.0 \times 10^{-5} \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
So as concentration doubles (from 0.25 to 0.50 ), the rate increases by $\left(1.5 \times 10^{-4}\right) /\left(7.0 \times 10^{-5}\right)=2.17$, so reaction is first order wrt $\mathrm{SO}_{2} \mathrm{Cl}_{2}$.
f) rate $=\mathrm{k}\left[\mathrm{SO}_{2} \mathrm{Cl}_{2}\right] ; \mathrm{k}=1.53 \times 10^{-4} / 0.50=3.1 \times 10^{-4} \mathrm{~s}^{-1}$
2.

a) $(0.40-0.20) / 20=0.010 \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
b) $(0.288-0.114) / 30=0.0058 \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
c) $(0.134-0.036) / 30=0.0033 \mathrm{moldm}^{-3} \mathrm{~s}^{-1}$
d) As $\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]$ doubles, rate increases by 1.75 so order wrt $\mathrm{H}_{2} \mathrm{O}_{2}=1$

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\text { Rate }=\mathrm{k}\left[\mathrm{H}_{2} \mathrm{O}_{2}\right], \mathrm{k}=0.025 \mathrm{~s}^{-1}
$$

3. 


$\left[\mathrm{NO}_{2}\right]=0.010$, rate $=5.7 \times 10^{-5}$
$\left[\mathrm{NO}_{2}\right]=0.050$, rate $=1.7 \times 10^{-5}$
$\left[\mathrm{NO}_{2}\right]=0.025$, rate $=3.9 \times 10^{-6}$
As $\left[\mathrm{NO}_{2}\right]$ doubles, rate increases by apprimxately 3.9 so reaction is second order wrt $\mathrm{NO}_{2}$ Rate $=\mathrm{k}\left[\mathrm{NO}_{2}\right]^{2}, \mathrm{k}\left(\right.$ from $1^{\text {st }}$ measurement $)=2.3 \mathrm{~mol}^{-1} \mathrm{dm}^{3} \mathrm{~s}^{-1}$

## Topic 11 Exercise 3

1. The slowest step in a chemical reaction
2. The coefficients of a chemical reaction show the total number of each species reacting in all the steps; the orders of reaction show the species reacting in the rate determining step only
3. The coefficients of the equation do not match the orders of reaction, which means the rate determining step cannot be the only step. In addition, there are 13 species in the chemical equation, which is much too many for a single step ( 3 is the maximum number of species which can collide in a single step)
4. Rds: $\mathrm{NO}_{2}+\mathrm{NO}_{2} \rightarrow \mathrm{NO}_{3}+\mathrm{NO}$

Then $\mathrm{NO}_{3}+\mathrm{CO} \rightarrow \mathrm{NO}_{2}+\mathrm{CO}_{2}$
5. Step 1: $\mathrm{X}+\mathrm{X} \rightarrow \mathrm{Z}$ (slow)

Step 2: $\mathrm{Z}+\mathrm{Y} \rightarrow \mathrm{W}+\mathrm{X}$ (fast)
Total: $\mathrm{X}+\mathrm{Y} \rightarrow \mathrm{W}$ ( Z made in step 1 is used in step 2, one of the X s used in step 1 is reformed in Step 2) species in rds $=2 \mathrm{xX}$ so rate $=\mathrm{k}[\mathrm{X}]^{2}$
6. $2 \mathrm{NO} \rightarrow \mathrm{N}_{2} \mathrm{O}_{2}$
$\mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$

## Topic 11 Exercise 4

1. i) $\mathrm{p}\left(\mathrm{N}_{2} \underline{\mathrm{O}}_{4}\right) \quad \mathrm{Pa}^{-1}$ ii) $\mathrm{p}\left(\mathrm{CH}_{3} \underline{C H}_{2} \underline{C O}_{2} \underline{\mathrm{CH}}_{2} \underline{C H}_{3}\right) \mathrm{p}\left(\mathrm{H}_{2} \underline{\mathrm{O})}\right.$ no units $\left(\mathrm{p}\left(\mathrm{NO}_{2}\right)^{2}\right)$ $\mathrm{p}\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H}\right) \mathrm{p}\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}\right)$
iii) $\quad(\mathrm{p}(\mathrm{HI}))^{2}$ no units $\mathrm{p}\left(\mathrm{H}_{2}\right) \mathrm{p}\left(\mathrm{I}_{2}\right)$
iv) $\frac{\left(\mathrm{p}_{\left.\left(\mathrm{SO}_{3}\right)\right)^{2}}^{\left(\mathrm{p}\left(\mathrm{SO}_{2}\right)\right)^{2} \mathrm{p}\left(\mathrm{O}_{2}\right)} \mathrm{Pa}^{-1} \mathrm{~A}\right.}{}$
v) $\quad\left(\mathrm{p}\left(\mathrm{NH}_{3}\right)\right)^{2} \quad \mathrm{~Pa}^{-2}$ $\mathrm{p}\left(\mathrm{N}_{2}\right)\left(\mathrm{p}\left(\mathrm{H}_{2}\right)\right)^{3}$
2. $\quad 2.96 \mathrm{kPa}$
3. 0.218 kPa
4. $\quad 56.2$
5. $\quad 133.3 \mathrm{kPa}$
6. $\quad 0.0607 \mathrm{MPa}^{-2}$
7. $0.86 \mathrm{kPa}^{-1}$
8. $\quad 4.2 \mathrm{kPa}$
9. $4.03 \times 10^{-5} \mathrm{kPa}^{-2}$
10. 80 kPa
