Class 3

Reviewing integrals

$$\int dx = x + c$$

$$\int x\, dx = \frac{x^2}{2} + c$$

$$\int x^2\, dx = \frac{x^3}{3} + c$$

$$\int x^n\, dx = \frac{x^{n+1}}{n+1} + c$$

$$\int \frac{1}{x}\, dx = \ln x + c$$

$$\int \frac{1}{x^2}\, dx = \int x^{-2}\, dx = \frac{x^{(-2+1)}}{(-2+1)} + c$$

$$= \frac{x^{-1}}{-1} + c = \frac{-1}{x} + c$$

use this

Revisiting compound interest

$$P = P_0 \left(1 + \frac{r}{n}\right)^{nt}$$

P_0 is initial amount

P is total amount at time t

r is the rate of interest ($\Rightarrow 0.05$ for 5%). ...

n is the number of times compounded

(e.g. $n = 2$ times a year for $t = 5$ years)

We can rewrite this as

$$P = P_0 \left(1 + \frac{rt}{nt}\right)^{nt} = P_0 \left(1 + \frac{x}{y}\right)^{y}$$

where $x = rt$ & $y = nt$

We use $\lim_{y \to \infty} \left(1 + \frac{x}{y}\right)^{y} = e^{x}$

$$P = P_0 e^{rt}$$ when the compounding is instantaneous.

Real reactions:

Making approximations

Eg:

$$\text{rate} = k[A]^n [B]^m [C]^p$$

if we start with $[A]_0$, $[B]_0$ & $[C]_0$

& we use small amounts of

$[A]_0$, then $[B]_0 \gg [A]_0$

$[C]_0 \gg [A]_0$

we can assume that as $[A]_0 \rightarrow [A]$

$[B] \approx [B]_0$

$[C]_0 \approx [C]_0$

$$\Rightarrow \boxed{\text{rate} = k'[A]^n}$$

where $k' = k[B]_0^m [C]_0^p$ etc.

Consider

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

the known rate $= k[NO_2]^2$

∴ the reaction is not <u>elementary</u>

<u>Molecularity</u> is the number of species that must collide to form products

$$A + B \rightarrow products$$

if rate $= k[A][B]$

then this is an <u>elementary</u> reaction with a molecularity of $\underline{2}$

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

$$\text{rate} = k[NO_2]^2$$

perhaps

$$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$

$$\rule{8cm}{0.5pt}$$

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

→ slow (rate limiting)

→ fast
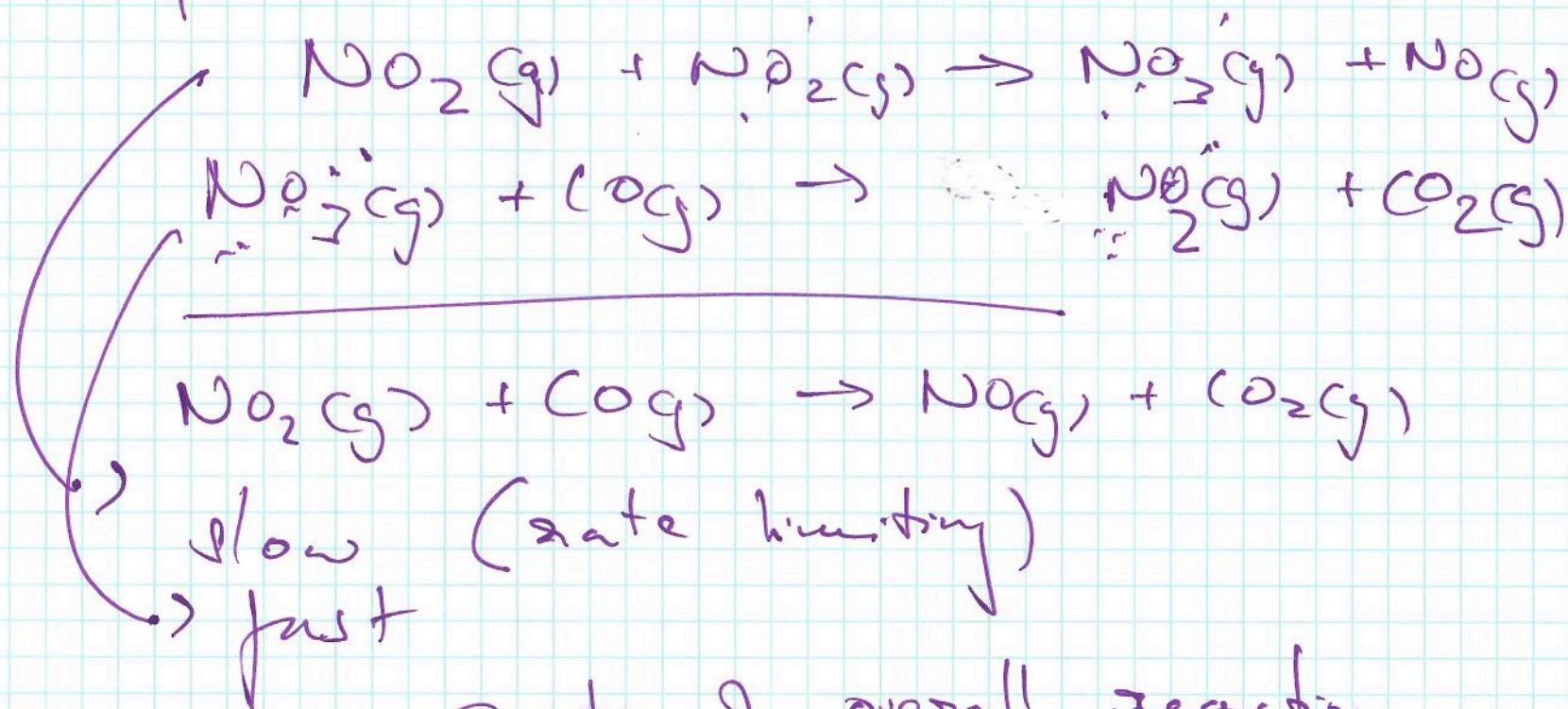
rate of overall reaction

is

$$\frac{d[NO_3]}{dt} = k[NO_2]^2$$

Forward & reverse first steps

$$2O_3 (g) \rightarrow 3O_2 (g)$$
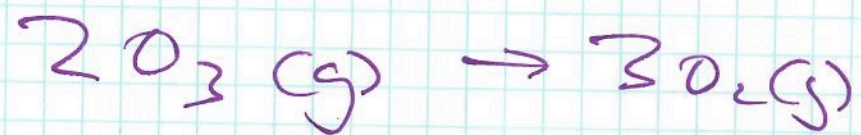
observed rate is $\dfrac{k [O_3]^2}{[O_2]}$

note that the product (O_2) enters the rate law

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$$

$$O + O_3 \overset{k_2}{\rightarrow} 2O_2$$
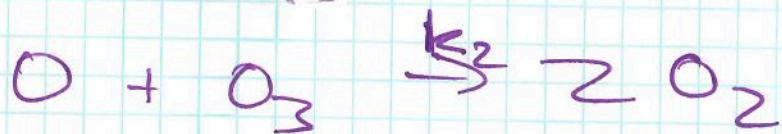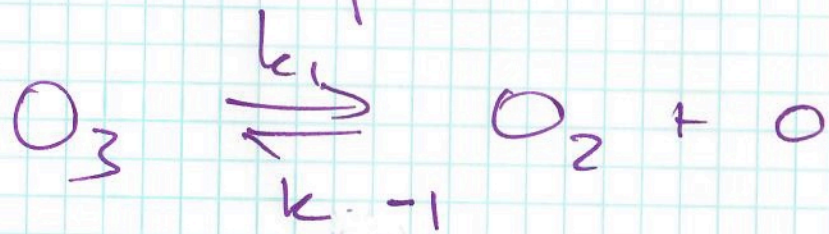
Overall rate $= k_2 [O][O_3]$

if the second reaction is rate limiting

then $[O] = \dfrac{k_1 [O_3]}{k_{-1} [O_2]}$ $\left(k_1 [O_3] = k_{-1} [O][O_2] \right)$

$$\text{rate} = k_2 [O][O_3] = k_2 \frac{k_1 [O]_3}{k_{-1} [O_2]} [O_3]$$

$$= k \frac{[O_3]^2}{[O_2]} \quad \left(k = \frac{k_2 k_1}{k_{-1}} \right)$$

$$Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$$

from expt $\text{rate} = k [Cl_2]^{1/2} [CHCl_3]$

proposed reaction:

$$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g)$$

$$Cl(g) + CHCl_3(g) \overset{k_2}{\longrightarrow} HCl + CCl_3(g)$$

$$CCl_3(g) + Cl(g) \overset{k_3}{\longrightarrow} CCl_4$$
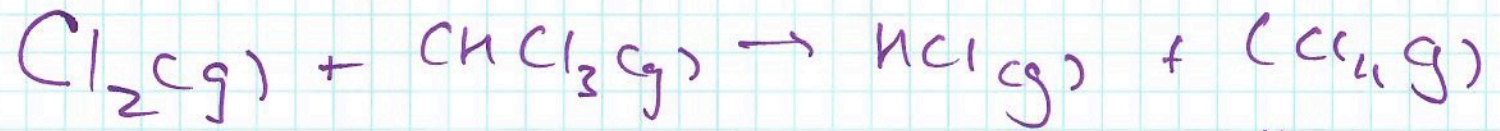
$$\text{rate} = k_2 [O][O_3] = k_2 \frac{k_1 [O]_3}{k_{-1} [O_2]} [O_3]$$

$$= k \frac{[O_3]^2}{[O_2]} \left(k = \frac{k_2 k_1}{k_{-1}} \right)$$

$$Cl_2(g) + CHCl_3(g) \longrightarrow HCl(g) + CCl_4(g)$$

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$$CCl_3(g) + Cl(g) \overset{k_3}{\longrightarrow} CCl_4$$
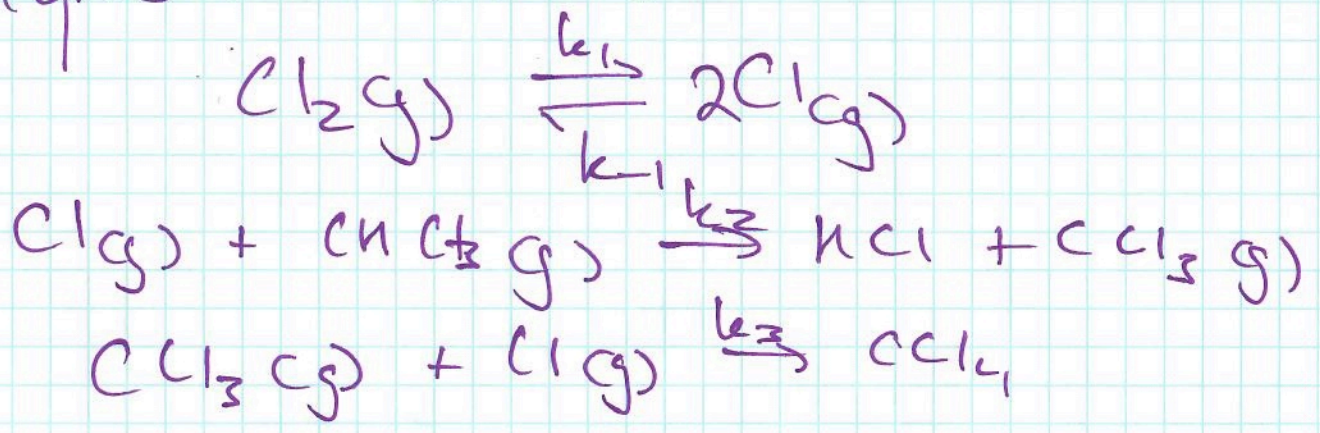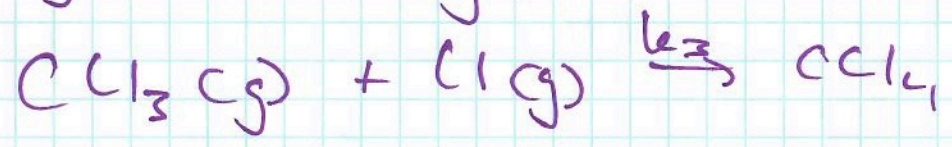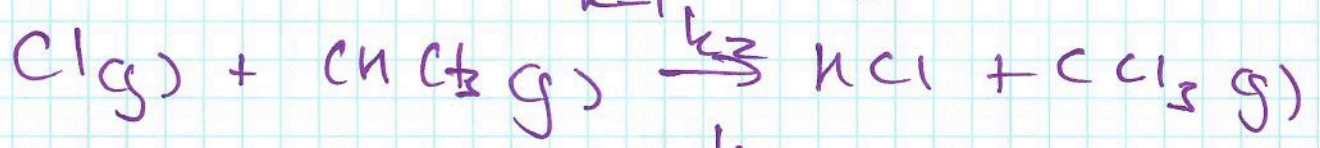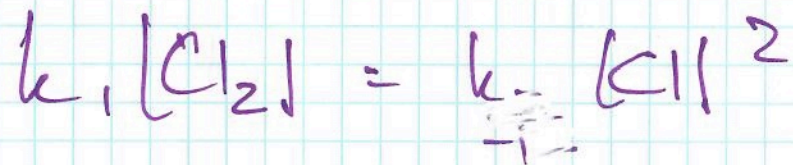
1 check : Overall reaction is balanced

2. lets assume the first reaction is
very rapid, and at equilibrium

$$k_1 [Cl_2] = k_{-1} [Cl]^2$$

$$[Cl] = \left(\frac{k_1 [Cl_2]}{k_{-1}} \right)^{1/2}$$

rate $= k_2 [Cl][CHCl_3]$

$$\boxed{k = k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2}} \qquad = k_2 \left(\frac{k_1}{k_{-1}} \right)^{1/2} [Cl_2]^{1/2} [CHCl_3]$$
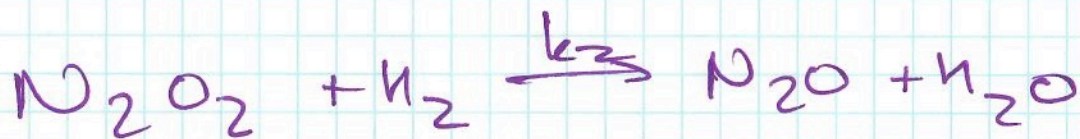
$$= k [Cl_2]^{1/2} [CHCl_3] \quad \checkmark$$

The steady state approximation.

concentration of an intermediate, M
is constant during the reaction

$$\frac{d[M]}{dt} = 0$$

e.g.

$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$$

$$\overline{2NO_{(g)} + H_2{(g)} \longrightarrow N_2O_{(g)} + H_2O_{(g)}}$$

$[N_2O_2]$ is the intermediate

$[N_2 O_2]$ is produced and lost

production $\dfrac{d[N_2 O_2]}{dt} = k_1 [NO]^2$

loss $\dfrac{d[N_2 O_2]}{dt} = k_{-1}[N_2 O_2] + k_2 [N_2 O_2][H_2]$

no net production or loss

$$\Rightarrow \quad k_1 [NO]^2 = k_{-1}[N_2 O_2] + k_2 [N_2 O_2][H_2]$$

$\underbrace{}_{\text{production}} \qquad \underbrace{\phantom{k_{-1}[N_2 O_2] + k_2 [N_2 O_2][H_2]}}_{\text{consumption}}$

$$k_1 [NO]^2 = [N_2 O_2]\left(k_{-1} + k_2 [H_2]\right)$$

$$[N_2 O_2] = k_1 [NO]^2 / \left(k_{-1} + k_2 [H_2]\right)$$

rate of reaction $= k_2[N_2O_2][H_2]$

$$= \frac{k_2 k_1 [H_2][NO]^2}{k_{-1} + k_2[H_2]}$$

approximations: if $k_2[H_2]$ is very large because $[H_2]$ is large

then the rate $\approx \frac{k_2 k_1 [H_2]}{k_2[H_2]}[NO]^2 = k_1[NO]^2$

\# if $[H_2]$ is very small then

$k_{-1} + k_2[H_2] = k_{-1} \Rightarrow$ rate $\approx \frac{k_2 k_1}{k_{-1}}[H_2][NO]^2$

$\approx k[H_2][NO]^2$

Temperature dependence of the
rate constant k

$$k = A e^{-E_a/RT}$$

Arrhenius

$$\ln k = \ln A - \frac{E_A}{RT}$$

$$\text{slope} = \boxed{-\frac{E_A}{R}}$$