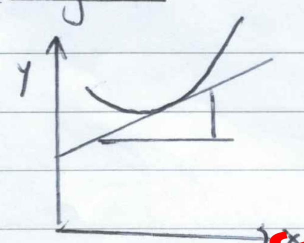
Physical Chemistry 152

Intro

- Rxns either fast / slow
- Thermodynamics explain where EQ position is
- Kinetics = Determines how ~~fast~~ quickly you get there.
  - Kinetics - work out detailed mechanisms of chemical processes
- Mechanism = Sequence of elementary steps - can't be broken → simpler ones.
- Mechanisms = Unimolecular, bi & termolecular (1, 2 & 3 molecules)
- Most important gas phase elementary steps = Bimolecular.

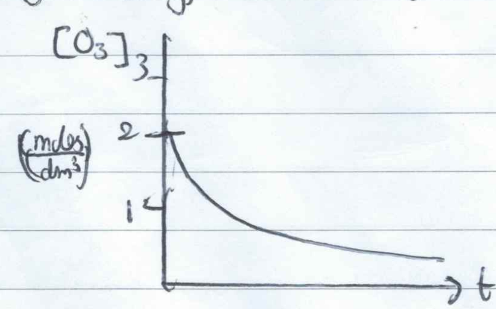
Rate of Rxn

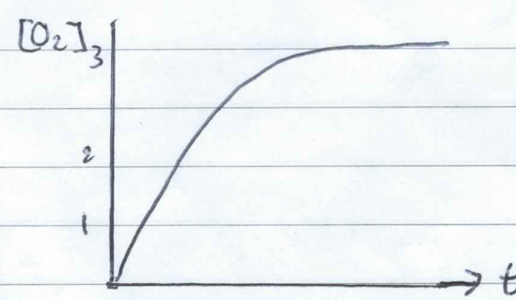


$\frac{dy}{dx}$ = rate

- Rate = How quickly conc of a reactant/product changes with time.

e.g. $2O_{3(g)} \longrightarrow 3O_{2(g)}$





- $2O_3 \rightarrow 3O_2$

$$-\frac{1}{2}\frac{d[O_3]}{dt} = +\frac{1}{3}\frac{d[O_2]}{dt}$$

(+) = Product
(−) = Reactant.

- Either = definition of rate of rxn.

Second Order

- When the rate equation = $k[A][B]$ - conditions chosen ∴ $[A]=[B]$ throughout the experiment
- Rate equation = treated same as $k[A]^2$

The Integrated 2^{nd} Order Rate Equation

$$-\frac{d[A]}{dt} = k[A]^2$$

Proof

$$-\frac{d[A]}{[A]^2} = -k\,dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\left[-[A]^{-1}\right]_{A_0}^{A} = \left[-kt\right]_0^t$$

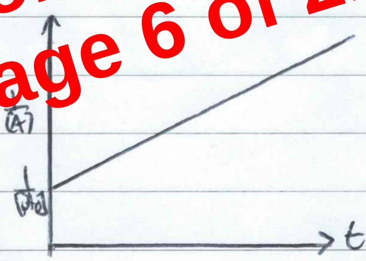
$$\therefore \frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Testing for 2^{nd} order kinetics

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$y = mx + c$$

$(m = k)$



- Straight line = test for 2^{nd} Order kinetics
- Find line of best fit
- Find gradient (k)

Half Life

- Half life ($t_{1/2}$) = time taken to use up half of the reactants.
- Zero Order; $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$, $t \propto \frac{1}{t_{\frac{1}{2}}}$ $t \uparrow$ as $\frac{1}{2}$ life $\downarrow$
- 2^{nd} Order ∴ $t_{1/2} = \frac{1}{k[A]_0}$ $t \uparrow$ as $\frac{1}{2}$ life $\uparrow$
- 1^{st} Order ∴ $t_{1/2} = \frac{\ln 2}{k}$
  - $t_{1/2}$ does not depend on $[A]_0$
  - Half life remains constant.
  - Use ∴ Iodine (Thyroid cancer) & Carbon (Carbon dating)

Eg How much of a 1×10^{-8} mol dm^{-3} Iodine sample is left after 4 weeks? ($\frac{1}{2}$ life = 8 days)?

8.07d = 697000s, 4w = 2419200s

A) $k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{697000} = \underline{9.94 \times 10^{-7}}$

$[A] = [A_0]e^{-kt}$

$[A] = 1 \times 10^{-8} \times e^{-9.94 \times 10^{-7} \times 2419200}$

$[A] = 9.03 \times 10^{-10}$ M left.