$2NH_3 \Leftrightarrow N_2 + 3H_2$

 $\Delta H = + 92 \text{ kJ mol}^{-1} \text{ at } 25 \text{ °C}$

 $K = [N_2][H_2]^3 / [NH_3]^2$ $2NH_3 \Leftrightarrow N_2 + 3H_2 \qquad K_1 (25 \circ C)$ $2NH_3 \Leftrightarrow N_2 + 3H_2 \qquad K_2 (100 \circ C)$

a) $K_2 > K_1$ b) $K_2 = K_1$ c) $K_2 < K_1$

L9

The rate of reaction

The rate of reaction

- is the change of the concentration of reactant
- divided by the time it takes for the change to occur
 - 3 mol dm⁻³ year ⁻¹
 - 5 mmol dm⁻³ s⁻¹



 Concentration of reactant decreases from 10 to 7, 10-7=3

• v=3/1

- The rate from 5.-6. second:
- Concentration of reactant decreases from 2 to 1, 2-1=1

• v=1/1



Rates are *measured*

- by following the time dependence of the concentration
- by spectroscopy, titration, conductivity, pH, and pressure or volume measurements

Zn(s) + 2HCl(aq) \rightarrow Zn²⁺(aq) + 2Cl⁻(aq) + H₂(g)



$(CH_3)_3C\text{-}Br(l) + H_2O(l) \rightarrow (CH_3)_3C\text{-}OH(l) + H^+(aq) + Br^-(aq)$



Figure 16.8 Conductometric monitoring of a reaction. When a reactant mixture differs in conductivity from the product mixture, the change in conductivity is proportional to the reaction rate. It is usually easier to monitor a nonionic reactant forming an ionic product.

Rate is measured by spectroscopy

starch + I_2 + amylase \rightarrow glucose + I_2 + amylase



Figure 10. A Spectrometric moitoring of a reaction. The investigato adds the reactant(s) to the sample tube and immediately places it in the spectrometer. For a reactant that is colored rate data is determined from a plot of light absorbed vs. time.



A first-order rate equation is rate = k₁[A]

 k_1 is the rate coefficient

The time dependence of the concentration is given by:

- $\ln[A] = -k_1t + \ln[A]_0$
- y = ax + b



- The *half-life* of a reaction is the time taken for the concentration to decrease to one half its initial value.
- Compare the halflife, t_{1/2}, that is necessary to achieve 1/2 [A]₀ at first and second graph
- Is it dependet upon
 [A]₀ value?



- $ln[A] = -k_1t + ln[A]_0$
- $\ln[A] \ln[A]_0 = -k_1 t$
- In { [A] / [A]₀} = $-k_1t$
- In { $\frac{1}{2}[A]_0 / [A]_0$ = $-k_1 t_{\frac{1}{2}}$
- (ln ¹/₂ = -ln 2)
- -In 2 = $k_1 t_{1/2}$
- $t_{1/2} = (\ln 2)/k_1 = 0.693/k_1$
- For a first-order reaction the half-life is independent of the initial concentration



x = time



Second-order rate equation

- rate = $k_2[A]^2$
- k₂ is the rate coefficient.
- The time dependence of the concentration is given by:
- $1/[A] = k_2 t + 1/[A]_0$
- y = ax + b



y = ax + b

 $1/[A] = k_2 t + 1/[A]_0$









Is it dependet upon
 [A]₀ value?





 $CH_3COCH_3(aq) + I_2(aq) P CH_2ICOCH_3(aq) + HI (aq)$

- $k_1 \text{ or } k_2$?
- A first-order rate equation is rate = k₁[A]
- A second-order rate equation is rate = $k_2[A]^2$

- The rate equation *cannot be predicted* from the chemical equation
- It must be determined experimentally

Iodination of propanone in acid solution

 $CH_3COCH_3(aq) + I_2(aq) P CH_2ICOCH_3(aq) + HI (aq)$

a) 2x c(CH₃COCH₃) Þ 2x v

b) $2x c(l_2) \ge v = const.$

c) $2x c(H^+) \ge 2x v$ from 0,1 to 0,2 M decrease from pH 1 to pH 0,7 $V = k_2 \times c(CH_3COCH_3) \times c(H^+)$

- Reactions often occur in several steps.
- If one step is much slower than the others it is termed the *rate-determining step*.
- A rate equation is explained by proposing a *mechanism* for the reaction, a sequence of individual reaction steps.

$CH_3COCH_3 + H^+ P CH_3COCH_4^+$

+ $I_2 \triangleright CH_2 ICOCH_3 + HI + H^+$

$v = k_2 \times c(CH_3COCH_3) \times c(H^+)$

- This is like two towns being joined by a good road crossing two bridges
- If the first bridge is narrow the traffic will queue to pass over it
- but once they are across, the second, broad bridge does not impede them

 $\begin{array}{c} \mathsf{CH}_3\mathsf{COCH}_3 + \mathsf{H}^+ \\ \mathrel{\triangleright} \mathsf{CH}_3\mathsf{COCH}_4^+ \end{array}$

+ I₂ Þ CH₂ICOCH₃ + HI + H⁺

If one step is much slower than the others it is termed the *rate-determining step*.





Arrhenius law

rate coefficient:

$$\mathbf{k} = \mathbf{A}\mathbf{e}^{-\mathbf{E}_{act}/\mathbf{RT}}$$

Eact, activation energy



 Many more molecules have at least E_a at high temperature then at low









 $CH_3COCH_3(aq) + I_2(aq) \ge CH_2ICOCH_3(aq) + HI(aq)$

2x c(H⁺) ▷ 2x v from 0,1 to 0,2 M decrease from pH 1 to pH 0,7



• Movie about E_a