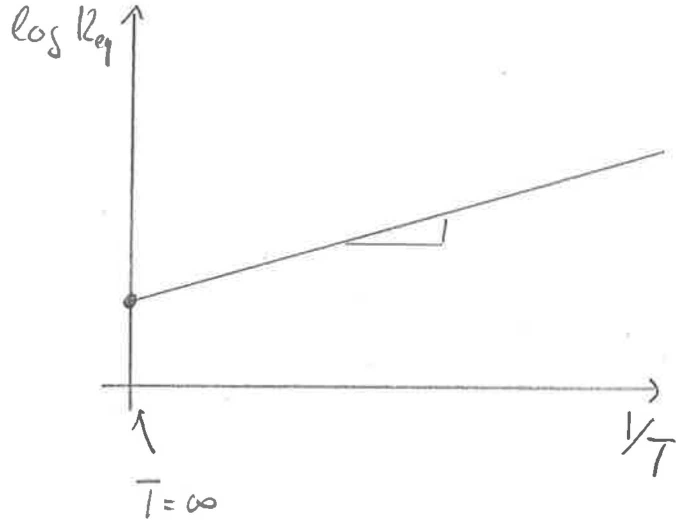
Reaction rates

2018-11-22

van't Hoff $\quad A + B \rightleftharpoons C$



$\log K_{eq}$ vs $\frac{1}{T} \Rightarrow$ linear

$$K_{eq} \sim e^{-\Delta H/kT}$$

ΔH = enthalpy change

$$\Rightarrow \frac{d \log K}{dT} = \frac{\Delta H}{kT^2}$$

· Gibbs free energy

$$\Delta G = \Delta H - T \Delta S$$

(enthalpy - entropic terms)

$$K_{eq} = e^{-\frac{\Delta G}{kT}}$$

· $T \to \infty \qquad \frac{\Delta G}{kT} = -\Delta S$

$\Rightarrow$ intercept above is ΔS ?

· the equilibrium is a balance of k_+ and k_-

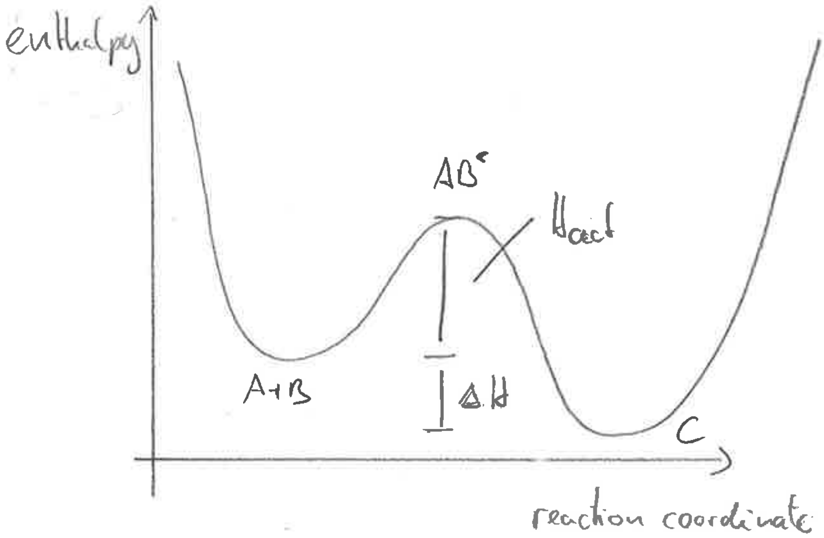
$$K_{eq} = \frac{k_+}{k_-} = e^{-\Delta G/kT}$$

$\Rightarrow$ at least one of $k_{\pm}$ needs to depend exponentially on $\frac{1}{T}$

- so far: diffusion limited rates
  - $k = 4\pi (D_A + D_B)(r_A + r_B)$
  - $D \sim \frac{kT}{r\eta}$

  $\Rightarrow$ linear temperature dependence

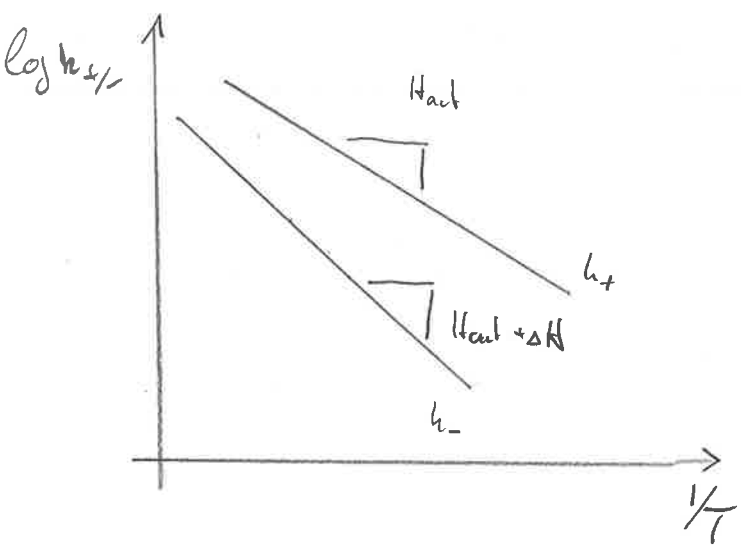
- instead of diffusion limited, rates can be reaction limited



- Barrier heigh Hact
- reaction energy ΔH

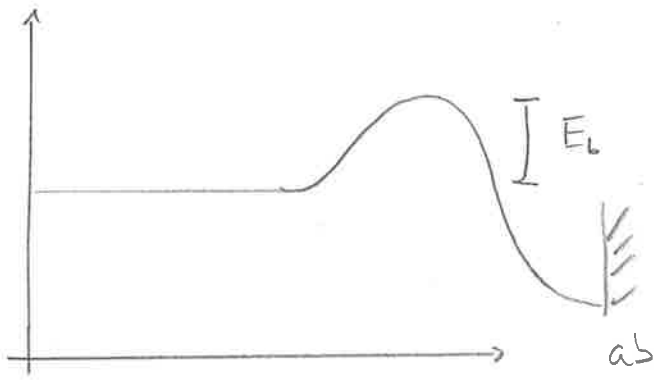
- rates to overcome barrier $k_+ \sim e^{-H_{act}/kT}$

$$k_- \sim e^{-\frac{H_{act} + \Delta H}{kT}}$$

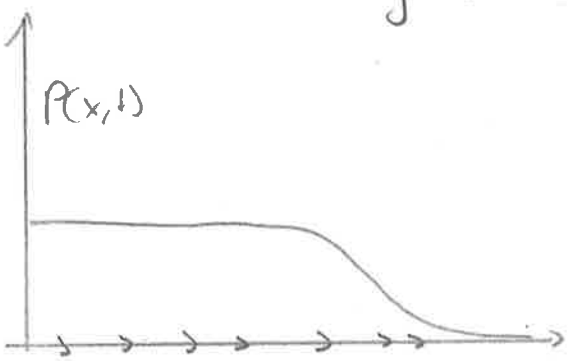


(rates increase with T)

Calculating barrier crossing rates



$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\underbrace{\left[-\mu kT\frac{\partial P}{\partial x} - \mu\frac{dE}{dx}P\right]}_{\text{flux}}$$



- essentially static
- constant flux

$$j = -\mu kT\frac{dP}{dx} - \frac{dE}{dx}P$$

$\Rightarrow$ attempt piece wise solution

• movement to generate flux $j \sim \frac{1}{\rho}$ $\Rightarrow$ flux unimportant before the barrier

$\Rightarrow$ dominant balance between

$\mu kT P'$ & $\mu E' P$

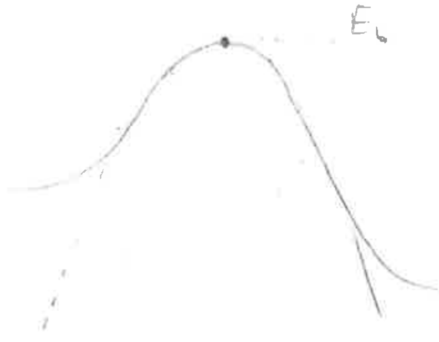
$\Rightarrow$ $P(x) \simeq e^{-(E(x)-E_a)/kT}$ before the barrier

$\Rightarrow$ not a good solution at the barrier

(it would predict $P(x)$ rises beyond the barrier,

$\rightarrow$ there, p-mass is carried away by the force into the absorbing boundary)

• at the boundary, we can approximate $E(x)$



$$E(x) \simeq E_b - \frac{ax^2}{2}$$

a = curvature

(center at $x=0$)

$$\Rightarrow \frac{dP(x)}{dx} = \frac{j}{\mu kT} + \frac{ax}{kT} P(x)$$

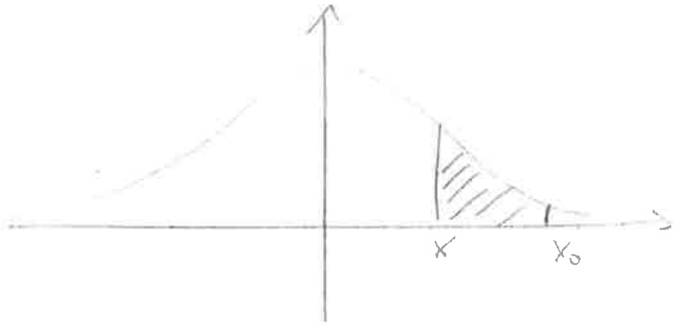
$$P(x) = \frac{j}{\mu kT} e^{\frac{ax^2}{2kT}} \int_{x_0}^{x} e^{-\frac{ay^2}{2kT}} dy$$

generates $ax\,\rho$

generates $\frac{j}{\mu kT}$

- boundary x_0 → integration constant
  → can use to fix boundary condition

- we need this to go to zero at the absorbing bc.
  ⇒ will happen at $x = x_0$ ⇒ $x_0 = b_c$.

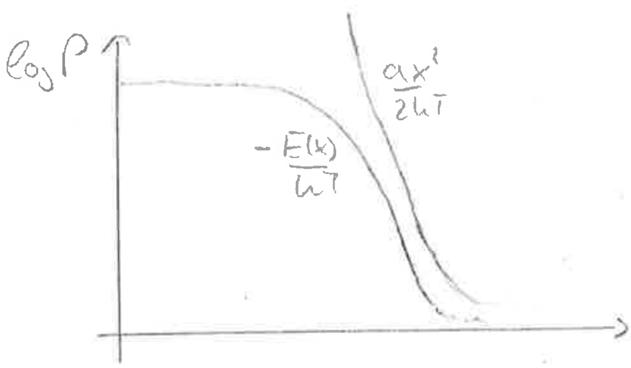


- at the other side of the boundary

$$P(x) \approx \frac{j}{\mu k T} e^{\frac{x^2 a}{2kT}} \sqrt{\frac{2\pi kT}{a}}$$ x before the bar

↑ entire gaussian integral

⇒ we need to match the two solutions



→ overlapping range of validity

→ prefactor j to match them up.

$$\frac{j}{\mu} \sqrt{\frac{2\pi}{kTa}}\, e^{\frac{x^2 a}{kT}} = c\, e^{-\frac{\overbrace{E(x) - E_b}^{\approx -\frac{a x^2}{2}} + \Delta E}{kT}} = c\, e^{-\frac{\Delta E}{kT} + \frac{a x^2}{2}}$$

E_∞

$$\Rightarrow \boxed{j = \mu k T c \sqrt{\frac{a}{2\pi k T}}\, e^{-\frac{\Delta E}{kT}}}$$ Kramer's rate for overdamped case

- what do the different parts mean?

c = contration at long distance

$c e^{-\Delta E / kT} \sim$ concentration of hopefuls

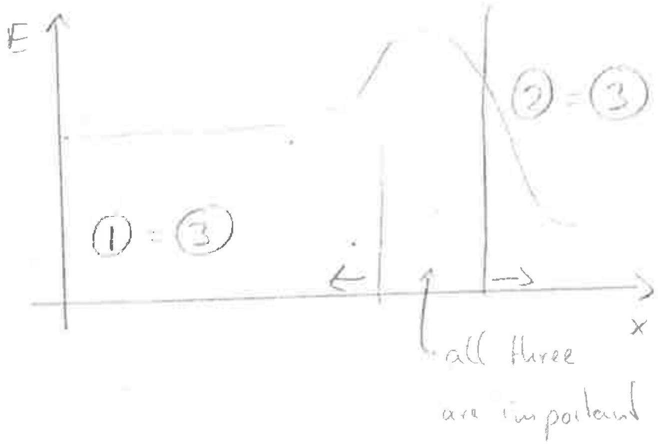
$D \sqrt{\frac{a}{2\pi kT}} \sim$ flux on top of the hill

↑
gradient
at the boundary

- the method of dominant balance

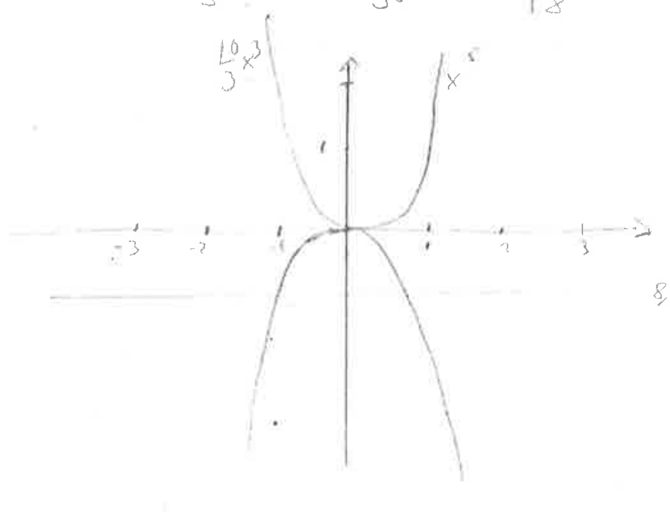
$$p' = \frac{j}{D} + \frac{E'}{kT} p$$

(1) (2) (3)



- dominant balance is a powerful method to obtain approximate solution.

$$18x^5 - 60x^3 + \frac{1}{5}x^2 = 8 \Rightarrow x^5 - \frac{10}{3}x^3 + \frac{1}{90}x^2 - \frac{8}{18} = 0$$



$\Rightarrow \frac{10}{3}x^3 = -\frac{8}{18}$

$\Rightarrow x^3 = -\frac{24}{180} = -\frac{8}{60}$

$\Rightarrow x \approx \frac{1}{2}$ $\left[x^5 = \frac{1}{32} \ll \frac{8}{18} \checkmark \right]$

$$\Rightarrow \quad 18x^5 = 60x^3$$

$$x^2 = \frac{10}{3} \approx 3.33$$

$$\Rightarrow \quad x_{2/3} = \pm 1.8$$

$x_1 = -0.52 \quad (0.511)$

$x_2 = -1.81 \quad (1.83)$ $\Rightarrow$ we got correct within a few percent!

$x_3 = -1.84 \quad (1.84)$