L37: review

Integrated steady-state flux at constant T:

$$J = - \frac{e^{\mu_g(x)/RT} - e^{\mu_g(0)/RT}}{\underbrace{\int_0^x dx' \, \frac{e^{\mu^\circ(x')/RT}}{RT\,u(x')}}_{>0}}$$

$J < 0 \Leftarrow \mu_g(x) > \mu_g(0)$

$c(0)$ increases; $c(x)$ decreases

$\Downarrow$

$\mu_g(x)$ decreases; $\mu_g(0)$ increases until

$\mu_g(x) = \mu_g(0)$ & $J = 0$

Thus, when a system goes out of equilibrium, the flux opposes the change until equilibrium is restored

"Le châtelier" (analogous to Newton's third law)

Today: - Flux in terms of Bayesian probabilities

- Transition state theory, part I

(where we make the opposite assumption from the usual, neglecting the $RT \ln c(x)$ term and letting μ° depend on coordinate instead.

Start be rewriting J a little, using:

1) $e^{\mu_g/RT} = e^{\frac{\mu^\circ + RT\ln c}{RT}} = c\,e^{\mu^\circ/RT}$

2) $RTu = D$; assume $D =$ constant

$$\Longrightarrow J = - \frac{D}{x} \, \frac{c(x)\,e^{\mu^\circ(x)/RT} - c(0)\,e^{\mu^\circ(0)/RT}}{\frac{1}{x}\int_0^x dx' \, e^{\mu^\circ(x')/RT}}$$

* note that in this and other formulas of μ we assume the solution/mixture is "ideal", i.e no attraction or repulsion exists between similar particles.

Also, $P_j = \dfrac{e^{-E_j/RT}}{\sum e^{-E_j/RT}}$ ⇒ Note the similarity between P_j and J in the previous page

$$J = -\frac{D}{x}\left\{ \underbrace{c(x)\,P(0|x)}_{\text{backward flux}} - \underbrace{c(0)\,P(x|0)}_{\text{forward flux}} \right\}$$

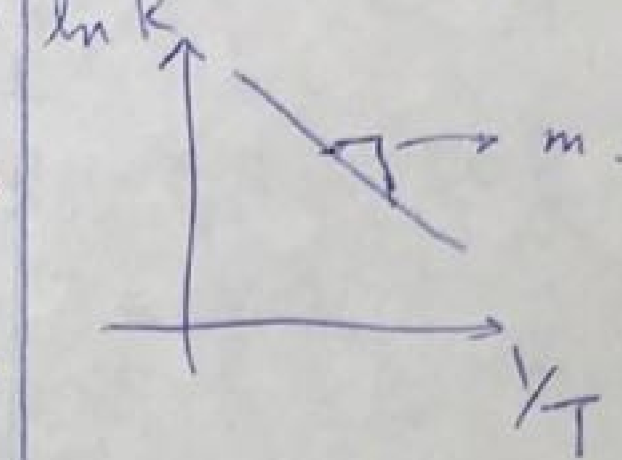
$P(0|x)$: Probability you end up at 0, having started at x

$P(x|0)$: Probability you end up at x having started at 0

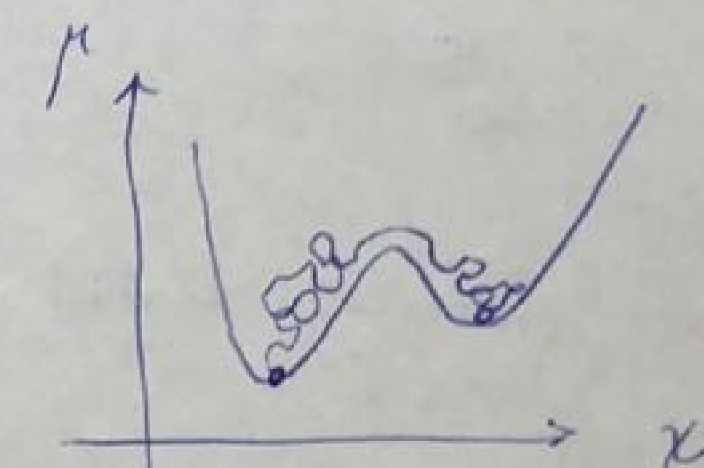
* the above formula is a general form of J and still holds if we had not made the previous assumptions (D = const. etc.)
* the formula above can also be used to model other transport phenomena such as vehicle traffic.

transition state theory

empirically, Arhenius discovered:



$m = -\dfrac{E_a}{R}$ $\Big\}$ $k = a \cdot e^{-E_a/RT}$

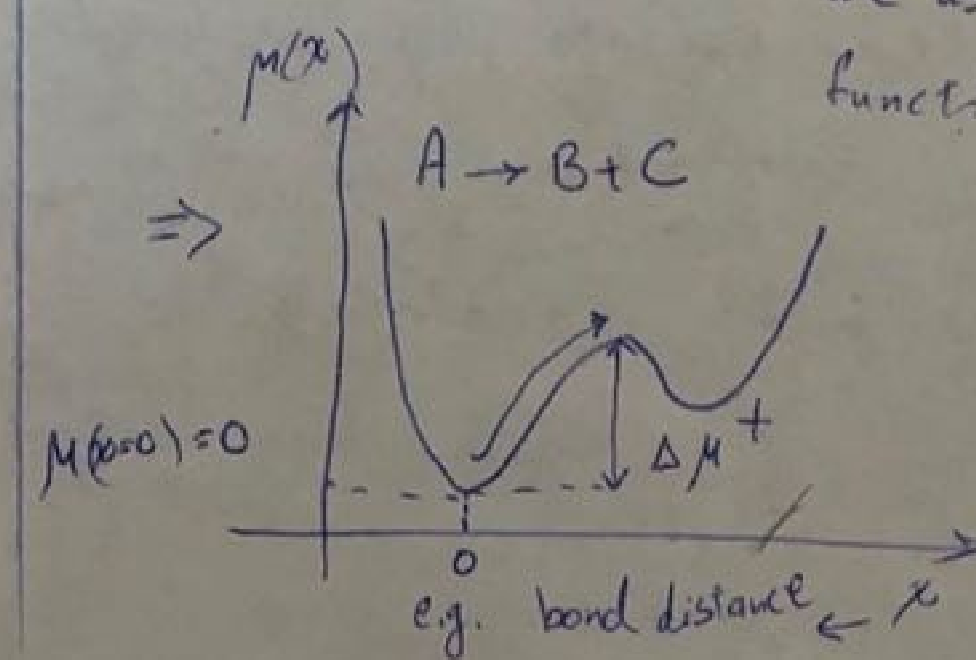


How could we derive this formula?

$\mu_g(x) = \mu^0(x) \equiv \mu(x)$

we assume μ is only a function of c and x

⇒



* Ensemble of molecules : what is k?

*note that unlike Arhenius we will derive the rate as a function of $\Delta\mu^+$ and not E_a; what makes $\Delta\mu^+$ positive is not solely due to the unfavorable ; breaking of a bond (positive ΔE) but also the unfavorable constraining of atoms in a configuration that reaction can occur ($\Delta S^+ > 0$)

$$\frac{J}{C(0)} = \overset{m/s}{v_F} = \frac{D}{x} \frac{e^{\mu(x=0)/RT}}{\frac{1}{x}\int_0^x dx' \, e^{\mu(x')/RT}}$$

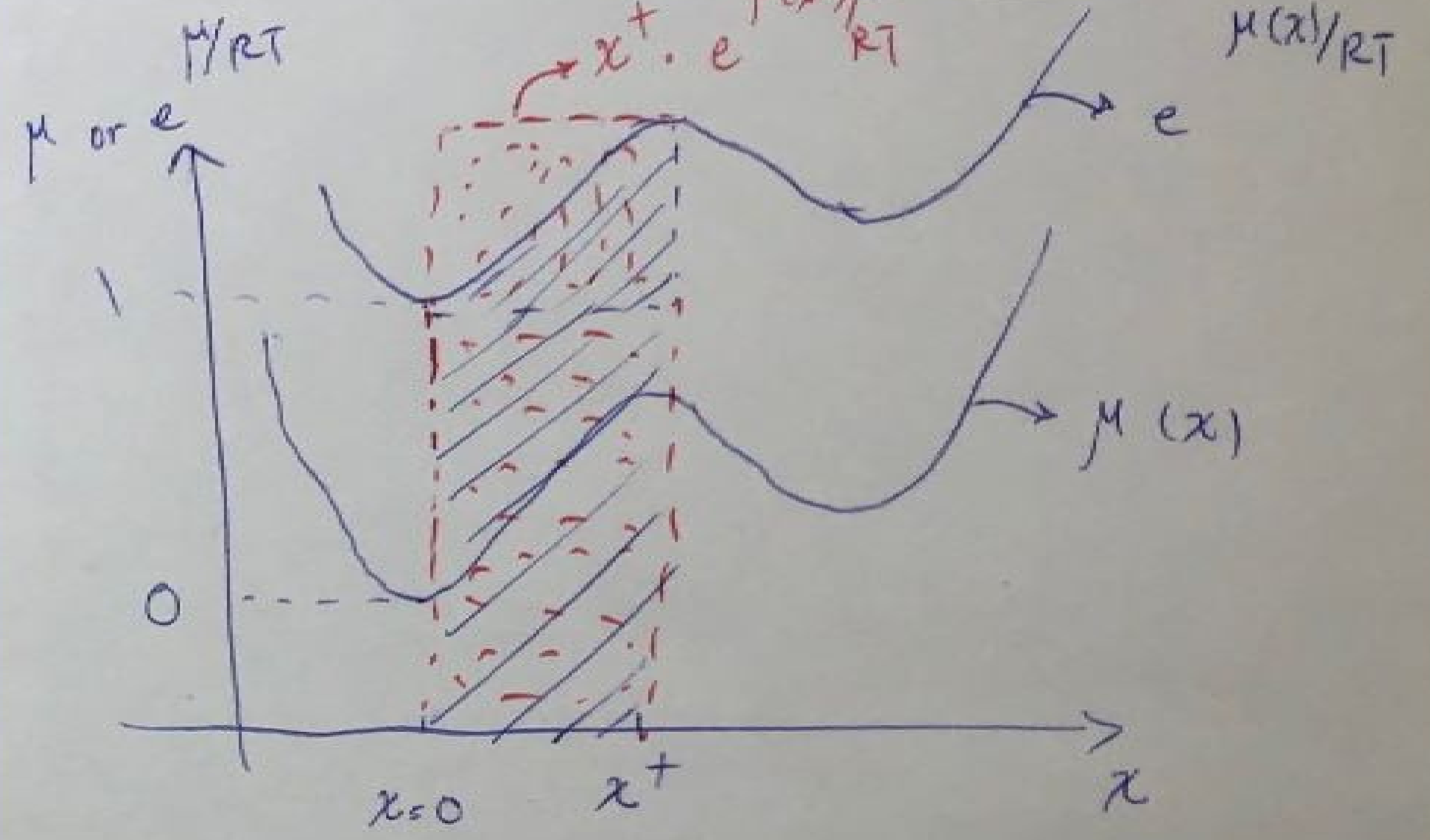
if $\mu(x=0)=0$ this becomes 1

let's do only the flux starting at $x=0$, not the reverse reaction

$\Downarrow$ $x = x^+$
set $\mu(x=0) = 0$

$$k_F = \frac{v_F}{x^+} = \frac{D}{x^{+2}} \frac{1}{\chi^{-1} e^{\mu(x^+)/RT}}$$

corrects that the $\int$ is always < the value of $e^{\mu(x^+)/RT}$ which is the max



* the blue hashed area is $\int_0^{x^+} dx \, e^{\mu(x)/RT}$, which is the denominator in the formula of v_F multiplied by x.

$$\chi = \frac{\text{area of hashed blue}}{\text{area of dotted red}} = \frac{\int_0^{x^+} dx \, e^{\mu(x)/RT}}{x^+ e^{\mu(x^+)/RT}}$$