

# 5. Chemical Equilibrium

## 1. Spontaneous chemical reactions



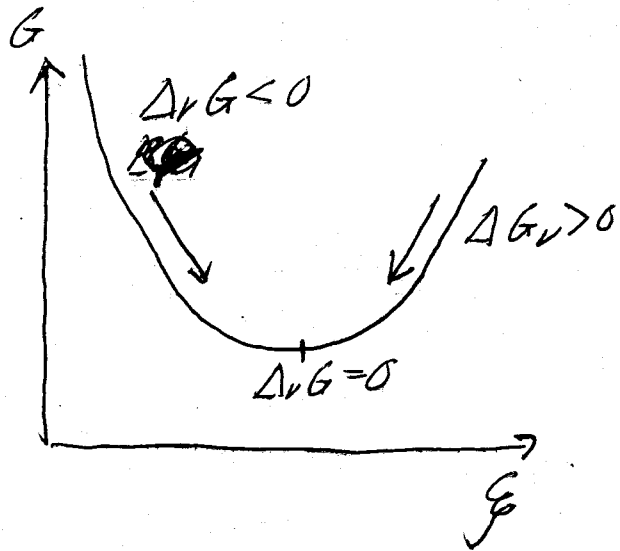
$\xi$ : extent of reaction

$$\boxed{dn_A = -d\xi = dn_B}$$

$$dG = \mu_A dn_A + \mu_B dn_B = (\mu_B - \mu_A) d\xi$$

Def.: reaction Gibbs energy

$$\boxed{\Delta_r G = \left. \frac{\partial G}{\partial \xi} \right|_{P,T} = \mu_B - \mu_A}$$



$\Delta_r G < 0$ :  
 reaction is spontaneous  
 $\Rightarrow$  exergonic

$\Delta_r G > 0$ :  
 reverse reaction is  
 spontaneous  $\Rightarrow$  endergonic

$\Delta_r G = 0$ : equilibrium

## 2. Description of equilibrium

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$$\begin{aligned} \Delta_r G &= \mu_B - \mu_A = (\mu_B^0 + RT \ln p_B) - (\mu_A^0 + RT \ln p_A) \\ &= \Delta_r G^0 + RT \ln \frac{p_A}{p_B} = \Delta_r G + RT \ln Q \\ &= Q \text{ reaction quotient} \end{aligned}$$

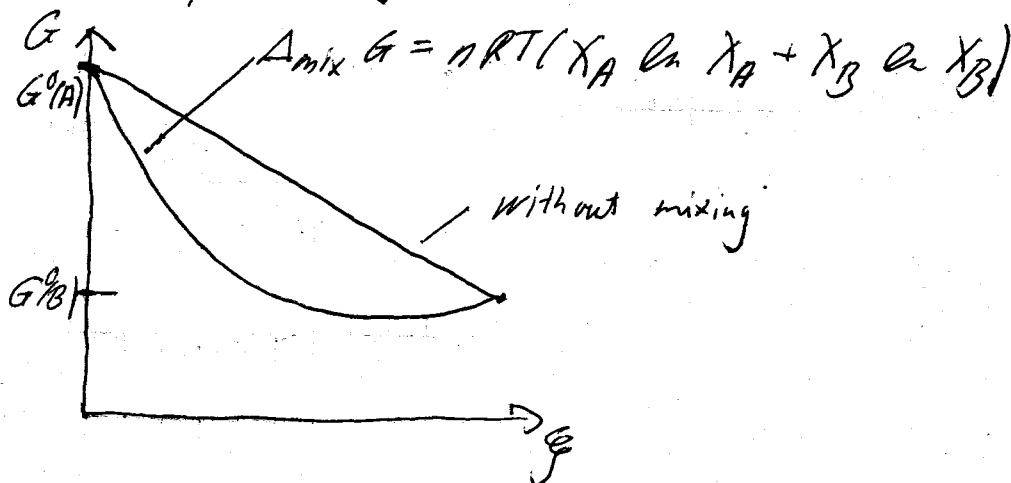
$$\begin{aligned} \Delta_r G^0 &= G_{B,m}^0 - G_{A,m}^0 = \mu_B^0 - \mu_A^0 = \\ &= \Delta_{\text{formation}} G^0(B) - \Delta_{\text{formation}} G^0(A) \end{aligned}$$

At equilibrium:

$$\Delta_r G = 0 \Rightarrow 0 = \Delta_r G^0 + RT \ln K$$

$$\Rightarrow \boxed{K = \frac{p_B}{p_A} \Big|_{\text{equilibrium}}} \quad \begin{array}{l} \text{equilibrium} \\ \text{constant} \end{array}$$

relevance of mixing:





Molecular interpretation:

$$K \sim e^{-\Delta_r G^0 / RT} = e^{-\Delta_r H / RT} e^{\Delta_r S / R}$$

3. Equilibria in biological systems

- ATP: • fuel of molecular motors and polymerization
- provides phosphate for phosphorylation

⇒ ATP hydrolysis at 37°C:

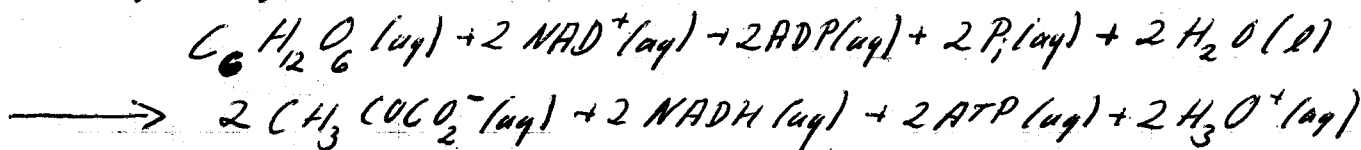


↑  
inorganic phosphate group

$$\Delta_r G = -30 \frac{\text{kJ}}{\text{mol}} \Rightarrow \text{exergonic}$$

ATP Production of ATP:

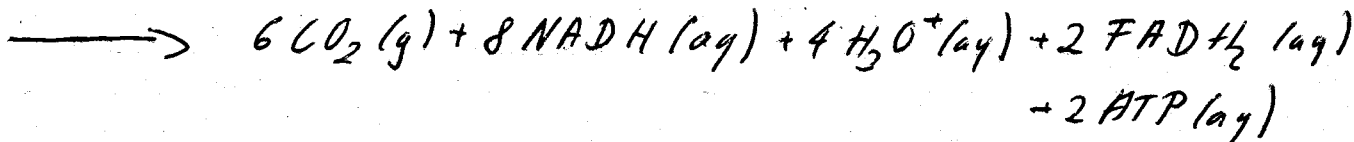
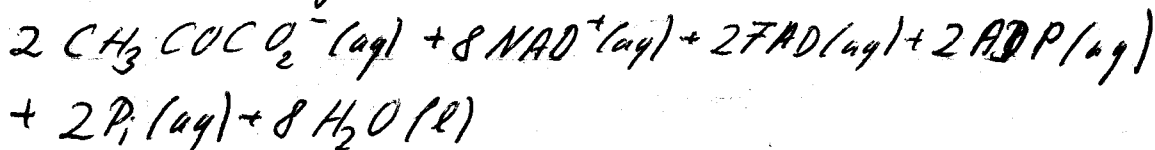
- glycolysis in the cytosol:



$$\Delta_r G = -87 \frac{\text{kJ}}{\text{mol}}$$

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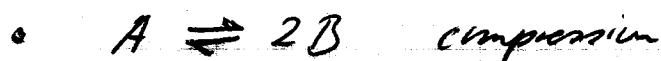
- citric acid cycle in mitochondria



## 4. Temperature and Pressure Dependence

### 4.1. pressure

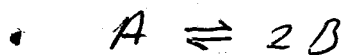
- by definition  $\left. \frac{\partial K}{\partial P} \right|_T = 0$



$$K = \frac{P_B^2}{P_A P^0} \Rightarrow \text{shift to } A \leftarrow 2B$$

- Le Chatelier's principle:

A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance



amount of A at equil:  $(1-\alpha)n$

" of B " " :  $2\alpha n$

$$X_A = \frac{(1-\alpha)n}{(1-\alpha)n + 2\alpha n} = \frac{1-\alpha}{1+\alpha} \quad X_B = \frac{2\alpha}{1+\alpha}$$

$$\Rightarrow K = \frac{P_B^2}{P_A P^0} = \frac{X_B^2 P}{X_A P^0} = \frac{4\alpha^2 P}{(1-\alpha^2) P^0}$$

$$\alpha = \left( \frac{1}{1 + 4 P / P^0 \cdot 1/K} \right)^{1/2}$$

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## 4.2. Temperature

The van't Hoff equation:

$$\ln K = - \frac{\Delta_r G^\circ}{RT}$$

$$\boxed{\frac{d \ln K}{dT} = - \frac{1}{R} \frac{d(\Delta_r G^\circ/T)}{dT} = - \frac{\Delta_r H^\circ}{RT^2}}$$

standard  
reaction  
enthalpy

$$\frac{d(1/T)}{dT} = - \frac{1}{T^2} \Rightarrow dT = -T^2 d(1/T)$$

$$\Rightarrow \boxed{\frac{d \ln K}{d(1/T)} = - \frac{\Delta_r H^\circ}{R}}$$

$\Rightarrow$  K at different temperatures:

$$\ln K_2 - \ln K_1 = \frac{1}{R} \int_{1/T_1}^{1/T_2} \Delta_r H^\circ d(1/T)$$

$\Delta_r H^\circ \approx T \text{ independent}$

$$\Rightarrow \boxed{\ln K_2 - \ln K_1 = - \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)}$$

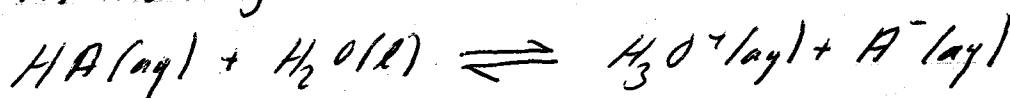
## 4.3 The pH

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$$pH = -\log a_{H_3O^+}$$

acid-base equilibria in water:

~~HA~~ (i) acidity constant



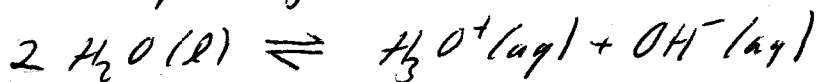
$$K_A = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} \Rightarrow pK_A = -\log K_A$$

(ii) basicity constant



$$K_B = \frac{a_{HB^+} a_{OH^-}}{a_B} \Rightarrow pK_B = -\log K_B$$

(iii) autoprotolysis



$$K_W = a_{H_3O^+} a_{OH^-} \quad pK_W = -\log K_W$$

$$pK_W = pH + pOH \quad \text{with } pOH = -\log a_{OH^-}$$

$$K_W = K_A K_B$$

acids

weak acids and bases: minimum lies close to reactants

- ⇒ proton transfer small
- ⇒ HA or B ≈ unchanged

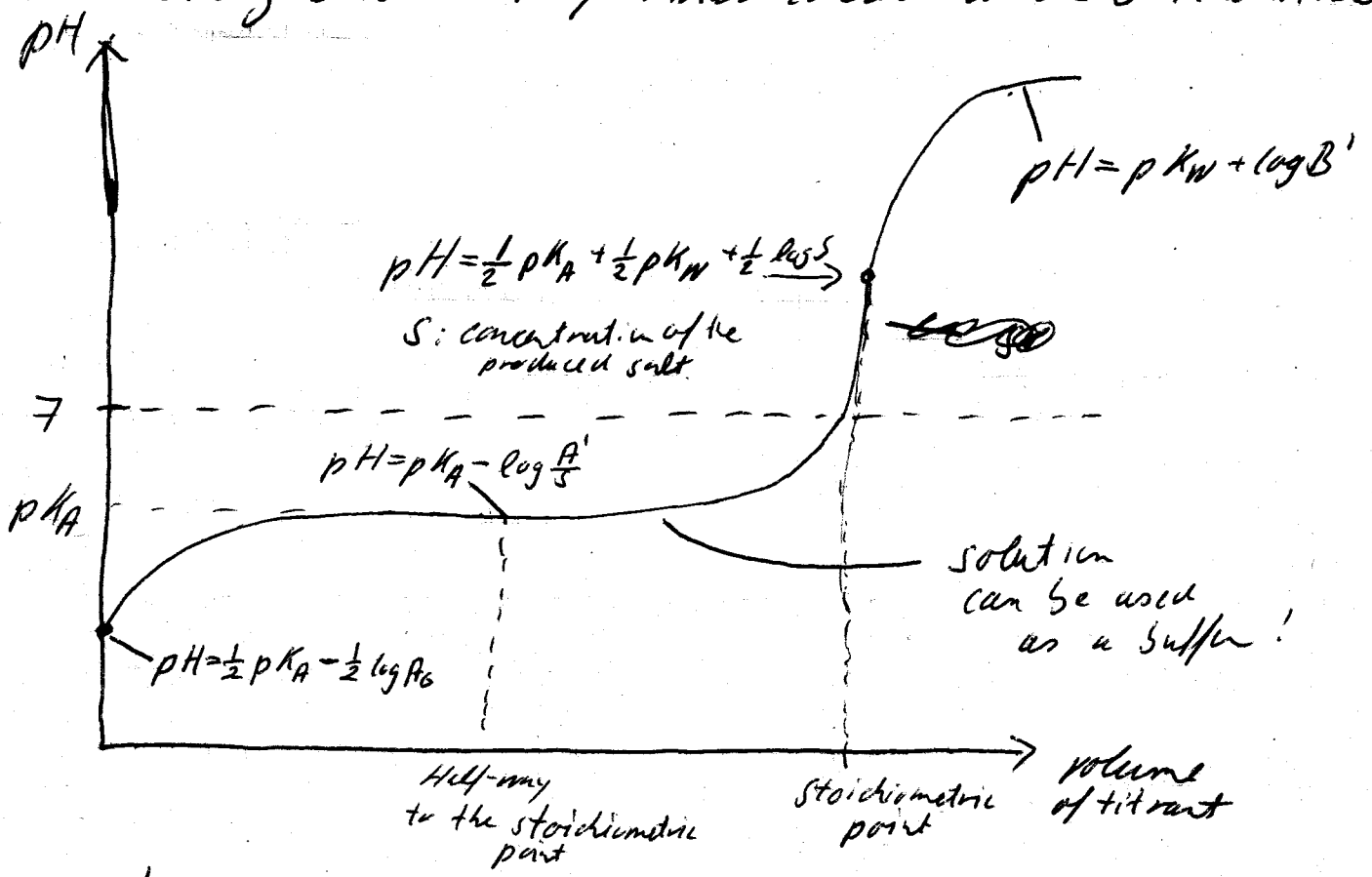
$$K_A \approx \frac{[H_3O^+]^2}{[HA]} \Rightarrow pH \approx \frac{1}{2} pK_A - \frac{1}{2} \log [HA]$$

$[H_3O^+] \approx [A^-]$

analog:  $pH = pK_w - \frac{1}{2} pK_B + \frac{1}{2} \log [B]$

Titration:

titrating a volume  $V_A$  of a weak acid of molar concentration  $A_0$  (the analyte) with a solution of a strong base MOH of molar concentration  $B$  (the titrant)



$$A' = A_0 \frac{V_A}{V} - S$$



# QM of Molecules

## 6. Quantum Theory - Introduction

### 6.1 Failures of classical physics

#### • Black body radiation

According to the equipartition theorem all the oscillators of the field share equally the energy supplied by the heated walls  $\Rightarrow$  even the highest frequencies  $\Rightarrow$  ultraviolet catastrophe

$\Rightarrow$  Planck:

oscillators are excited only if they can acquire an energy of at least  $h\nu$   
quantization of energy:  $E = n h \nu$

Planck's constant  
 $6.62608 \cdot 10^{-34} \text{ Js}$

#### • Heat capacities

##### Dulong and Petit's law (classical)

each atom can oscillate in three dimensions, the average energy of each atom is  $3kT$ , for  $N$  atoms:  $3NkT$

$$U_m = 3 N_A k T = 3 R T$$

$$C_{V,m} = \frac{\partial U_m}{\partial T} = 3 R$$

fails as ~~as~~ as  $T \rightarrow 0$

## Einstein:

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each atom oscillated about its equilibrium position with a single frequency and the energy of oscillation is confined to discrete values  $n h \nu$

$$\Rightarrow U_{\text{m}} = \frac{3 N_A h \nu}{e^{h \nu / k T} - 1} \Rightarrow C_{V, \text{m}} = 3 R f^2$$

$$f = \frac{\theta_E}{T} \left( \frac{e^{\theta_E / 2T}}{e^{\theta_E / T} - 1} \right)$$

Einstein temperature

$$\theta = \frac{h \nu}{k}$$

for  $T \gg \theta_E \Rightarrow$  classical result

$$\text{for } T \ll \theta_E: f \approx \frac{\theta_E}{T} \left( \frac{e^{\theta_E / 2T}}{e^{\theta_E / T}} \right) = \frac{\theta_E}{T} e^{-\theta_E / 2T}$$

$$f \rightarrow 0 \text{ for } T \rightarrow 0$$

- at low temperatures only a few oscillators possess enough energy to oscillate significantly
- at higher temperatures there is enough energy available for all oscillators to become active  
 $\Rightarrow$  classical value

Debye: range of discrete frequencies

$$C_{V, \text{m}} = 3 R f$$

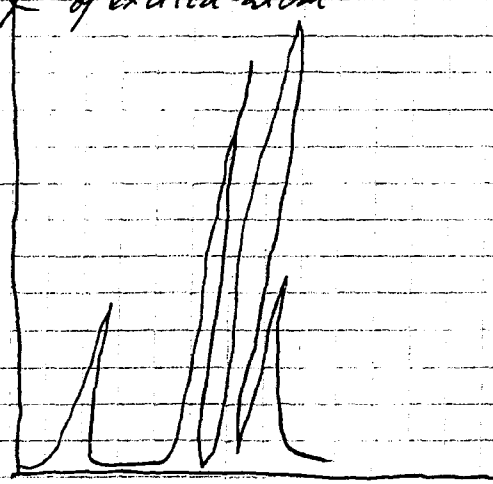
$$\theta_D = \frac{h \nu_D}{k}$$

$$f = 3 \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D / T} \frac{x^3 e^{-x}}{(e^x - 1)^2} dx$$

# Atomic and Molecular spectra

atomic spectra:

emission intensity  
of excited atom



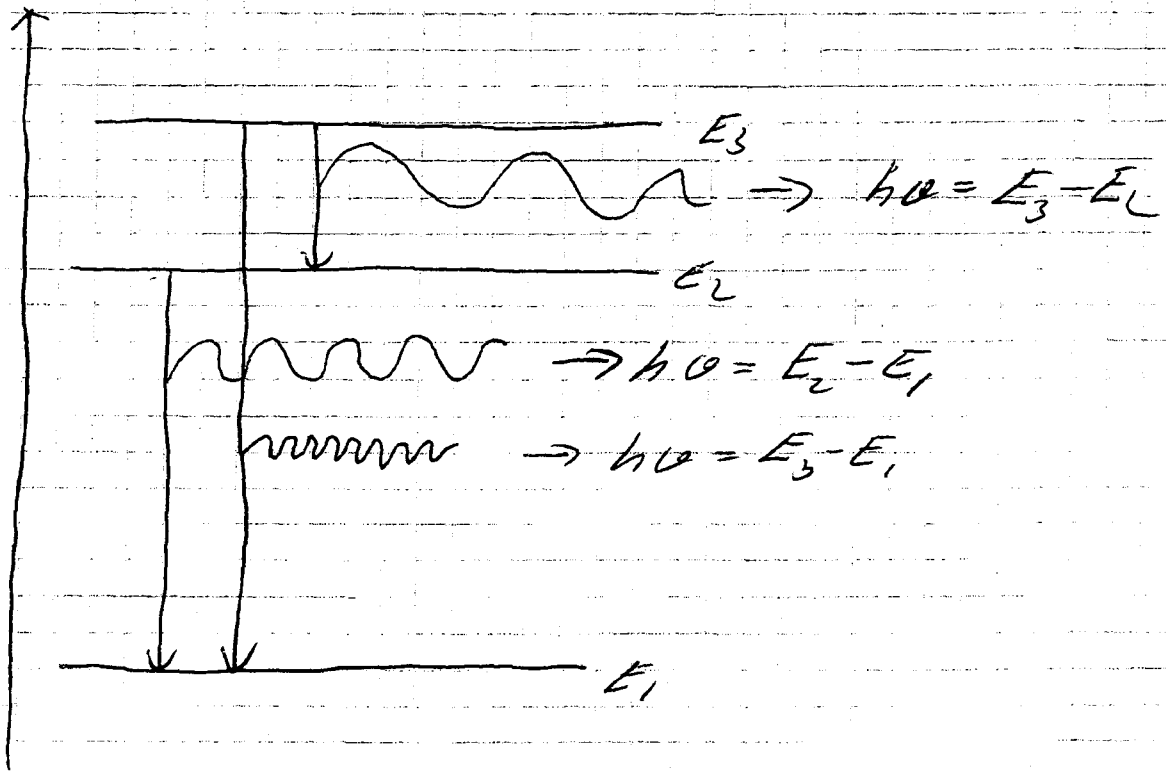
⇒ sharp lines

in absorption and emission

⇒ energy of atoms is

also confined to discrete values

⇒ energy can be emitted or absorbed only in discrete amounts



### Bohr Radius $a_0$ :

potentielle Energie des Elektrons hängt allein von seinem Abstand vom Kern ab

$$U(r) = - \frac{Z \cdot e^2}{(4\pi\epsilon_0) r}$$

$$a_0 = \frac{\hbar^2 4\pi\epsilon_0}{m_e \cdot e^2}$$

$$R_n = n a_0 \quad n = 1, 2, \dots$$

$$E_n = - \frac{e^4 m_e Z^2}{(4\pi\epsilon_0)^2 2\hbar^2 n^2}$$

### • Photoelectric effect

ejection of an electron when it is involved in a collision with a photon

$$\frac{1}{2} m_e v^2 = h\nu - \phi$$

↑ kinetic energy  $e^-$       ↓ photon      ← work function

### • Electron diffraction

⇒ electron microscopy

de Broglie wave length:  $\lambda = \frac{h}{p}$

The Schrödinger equation:  $\psi$ : wavefunction

1-dim  $-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi$

potential energy

$$\hbar = \frac{h}{2\pi}$$

3-dim  $-\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi = E \psi$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

spherical  $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2$

$$\Lambda^2 = \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta}$$

$$H \psi = E \psi$$

Hamiltonian operator  $= -\frac{\hbar^2}{2m} \nabla^2 + V$

time-dependent:

$$H \psi = i \hbar \frac{\partial \psi}{\partial t}$$

e.g.  $V(x) = V$

$$\frac{d^2 \psi}{dx^2} = -\frac{2m}{\hbar^2} (E - V) \psi$$

$$\Rightarrow \psi = e^{ikx} \quad \text{with } k = \left( \frac{2m(E-V)}{\hbar^2} \right)^{1/2}$$

$$E - V = E_{kin} \Rightarrow E_{kin} = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

$$\Rightarrow p = \hbar k = \frac{h}{\lambda} \quad \text{with } \lambda = 2\pi/k$$

Born interpretation: $\psi$  probability amplitude $|\psi|^2$  probability density

If the wavefunction of a particle has the value  $\psi$  at some point  $r$  then the probability of finding the particle in an infinitesimal volume  $d\tau = dx dy dz$  at that point is proportional to  $|\psi|^2 d\tau$

normalization  $\int |\psi|^2 d\tau = 1$

$\psi$ : continuous, continuous slope, single-valued, finite, cannot be zero every where