

Table 1: Key units in Physical Chemistry

N_{Av} :	6.02214×10^{23}	mol^{-1}		
1 amu:	1.6605×10^{-27}	kg		
k_{B} :	1.38065×10^{-23}	J K^{-1}	8.61734×10^{-5}	eV K^{-1}
R :	8.314472	$\text{J K}^{-1} \text{mol}^{-1}$	8.2057×10^{-2}	$\text{l atm mol}^{-1} \text{K}^{-1}$
σ_{SB} :	5.6704×10^{-8}	$\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$		
c :	2.99792458×10^8	m s^{-1}		
h :	6.62607×10^{-34}	J s	4.13566×10^{-15}	eV s
\hbar :	1.05457×10^{-34}	J s	6.58212×10^{-16}	eV s
hc :	1239.8	eV nm		
e :	1.60218×10^{-19}	C		
m_e :	$9.10938215 \times 10^{-31}$	kg	1: 0.5109989	MeV c^{-2}
ϵ_0 :	8.85419×10^{-12}	$\text{C}^2 \text{J}^{-1} \text{m}^{-1}$	5.52635×10^{-3}	$e^2 \text{\AA}^{-1} \text{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV \AA
a_0 :	0.529177×10^{-10}	m	0.529177	\AA
E_{H} :	1	Ha	27.212	eV

1 The Classical Foundations

1.1 Lecture 0: Introduction

1. Burning lighter
2. Foundations of Physical Chemistry
 - (a) Quantum mechanics
 - (b) Statistical mechanics
 - (c) Thermodynamics, kinetics, spectroscopy
 - (d) Physical and chemical properties of matter

1.2 Lecture 1: Basic statistics

1. Discrete probability distributions—Coin flip
 - (a) Example of Bernoulli trial, 2^n possible outcomes from n flips
 - (b) Number of ways to get i heads in n flips, ${}_nC_i = n!/i!(n-i)!$
 - (c) Probability of i heads $P_i \propto {}_nC_i$
 - (d) Normalized probability, $\tilde{P}_i = P_i / \sum_i P_i = {}_nC_i / 2^n$
 - (e) Expectation value $\langle i \rangle = \sum_i i \tilde{P}_i$
2. Continuous distributions—temperature
 - (a) Probability density $P(x)$ has units $1/x$
 - (b) Normalized $\tilde{P}(x) = P(x) / \int P(x) dx$
 - (c) (Unitless) probability $a < x < b = \int_a^b \tilde{P}(x) dx$

(d) Expectation value $\langle f(x) \rangle = \int f(x) \tilde{P}(x) dx$

(e) Mean = $\langle x \rangle$

(f) Mean squared = $\langle x^2 \rangle$

(g) Variance $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$

(h) Standard deviation $\Delta x = \sigma$

3. Boltzmann distribution

(a) $P(E) \propto e^{-E/k_B T}$, in some sense the definition of temperature

(b) Energy and its units

(c) Absolute temperature and its units

(d) $k_B T$ as an energy scale, 0.026 eV at 298 K

(e) Gravity example

i. $E(h) = mgh$, linear, continuous energy spectrum

ii. molecule vs car in a gravitational field (Table 2)

iii. Barometric law for gases, $P = P_0 e^{-mgh/k_B T}$

(f) Kinetic energy in 1-D example

i. $KE = \frac{1}{2} m v_x^2$

ii. $P_{1D}(v_x) = \left(\frac{m}{2\pi k_B T} \right)^{1/2} \exp \left(-\frac{m|v_x|^2}{2k_B T} \right)$

iii. Gaussian distribution, mean μ , variance σ^2

$$G(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left(-\frac{(x - \mu)^2}{2\sigma^2} \right)$$

iv. By inspection, $\mu = \langle v_x \rangle = 0$, $\sigma^2 = \langle v_x^2 \rangle = k_B T/m$

v. Molecule vs car again

(g) Equipartition – energy freely exchanged between all degrees of freedom

Table 2: Car vs gas molecule at the earth's surface

	car	gas molecule
m	1000 kg	1×10^{-26} kg
h	1 m	1 m
mgh	9800 J	9.8×10^{-26} J
	6.1×10^{22} eV	6.1×10^{-7} eV
T	298 K	298 K
$k_B T$	0.026 eV	0.026 eV
$mgh/k_B T$	2.4×10^{24}	2.3×10^{-5}
$P(1 \text{ m})/P(0)$	$e^{-2.4 \times 10^{-24}}$	0.99998
$\langle h \rangle$	0 m	42 km
$\langle v_x \rangle^{1/2}$	2×10^{-12} m/s	640 m/s

Table 3: Energy conversions and correspondences

	J	eV	Hartree	kJ mol^{-1}	cm^{-1}
1 J =	1	6.2415×10^{18}	2.2937×10^{17}	6.0221×10^{20}	5.0340×10^{22}
1 eV =	1.6022×10^{-19}	1	0.036748	96.485	8065.5
1 Ha =	4.3598×10^{-18}	27.212	1	2625.6	219474.6
1 kJ mol^{-1} =	1.6605×10^{-21}	0.010364	3.8087×10^{-4}	1	83.5935
1 cm^{-1} =	1.986410^{-23}	1.23984×10^{-4}	4.55623×10^{-6}	0.011963	1

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  RO = 8.31441    J/mol K
5  mass = 28. /1000  kg/mol N2
6
7  def Boltzmann(E,T):
8      return np.exp(E/(RO*T))/(RO*T)
9
10 def MB1D(v,T):
11     return np.sqrt(mass/(2*np.pi*RO*T))*np.exp((mass*v*v)/(2*RO*T))
12
13 def MB(c,T):
14     K = 0.5 * mass * c * c
15     degeneracy = 4 * np.pi * c * c
16     normalization = (mass/(2*np.pi*RO*T))**1.5
17     return normalization*Boltzmann(K,T)
18
19 energy = np.linspace(0,3000,1500)
20 velocity = np.linspace(1000,1000,1000)
21 speed = np.linspace(0,1500,1000)
22
23 plt.figure()
24 for Temperature in [100,300,1000]:
25     Probability = Boltzmann(energy,Temperature)
26     plt.plot(Probability,energy,label=0 K.format(Temperature))
27
28 legend = plt.legend()
29
30 plt.ylabel(Energy (J/mol))
31 plt.xlabel(Probability (mol/J))
32 plt.title(Boltzmann distribution at various temperatures)
33 plt.savefig(./Images/Boltzmann.png)
34
35 plt.figure()
36 for Temperature in [100,200,300,400,500]:
37     Probability = MB1D(velocity,Temperature)
38     plt.plot(velocity,Probability,label= K.format(Temperature))
39
40 legend=plt.legend()
41 plt.xlabel(Velocity (m/s))
42 plt.ylabel(Probability (1/(m/s)))
43 plt.title(Boltzmann distribution at various temperatures)
44 plt.savefig(./Images/MB1D.png)
45
46 plt.figure()
47 for Temperature in [100,200,300,400,500]:
48     Probability = MB(speed,Temperature)
49     plt.plot(speed,Probability,label= K.format(Temperature))
50
51 legend=plt.legend()
52 plt.xlabel(Speed (m/s))
53 plt.ylabel(Probability (1/(m/s)))

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54 plt.title(Boltzmann distribution at various temperatures)
55 plt.savefig('./Images/MB.png')

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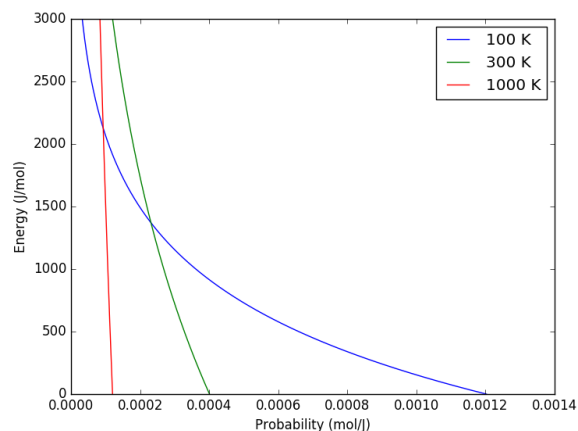


Figure 1: Boltzmann distribution at various temperatures

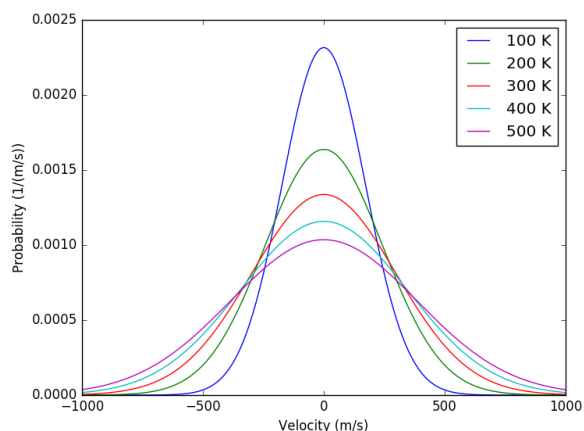


Figure 2: One-dimensional (Gaussian) velocities of N₂ gas

1.3 Lecture 2: Kinetic theory of gases

1. Postulates

- (a) Gas is composed of molecules in constant random, thermal motion
- (b) Molecules only interact by perfectly elastic collisions
- (c) Volume of molecules is \ll total volume

2. Maxwell-Boltzmann distribution of molecular speeds

- (a) Speed $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$

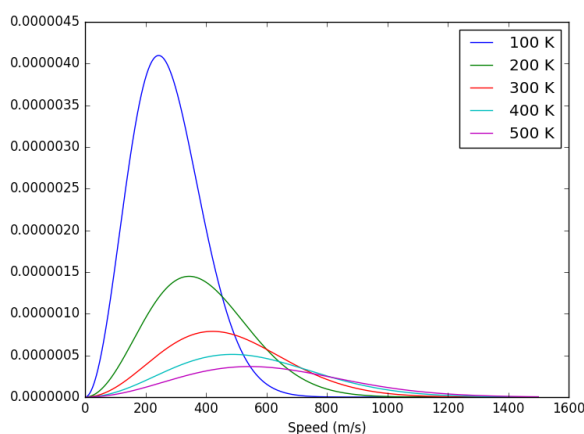


Figure 3: Maxwell-Boltzmann speed distribution of N_2 gas

(b) $P_{MB}(v)dv = P_{1D}(v_x)P_{1D}(v_y)P_{1D}(v_z) * \text{degeneracy}(v)dv$

(c) mean speeds $\propto \sqrt{T}$

(d) mean energy $U = \frac{3}{2}RT$ and heat capacity $C_v = \frac{3}{2}R$

3. Flux and pressure

(a) Velocity flux $j(v_x)dv_x = v_x \frac{N}{V} P(v_x)dv_x$, molecules /area /time / v_x

(b) Wall collisions, J_w , total collisions /area /time

(c) Momentum exchange, pressure, ideal gas law

4. Collisions and mean free path

(a) Collision cross section $\sigma = \pi d^2$, size of molecule

(b) Molecular collisions, z per molecule and z_{AA} per volume

(c) Mean free path, λ , mean distance between collisions

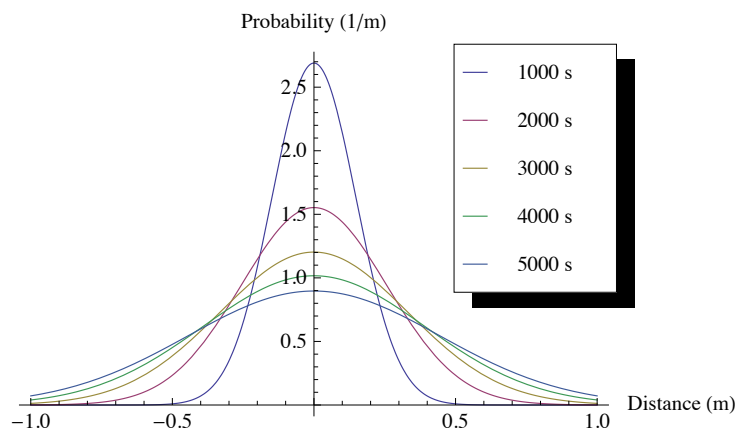


Figure 4: Diffusional spreading, $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

Table 4: Kinetic theory of gases key equations

Boltzmann distribution ($g(E)$: degeneracy of E)	$P(E) = g(E)e^{-E/k_B T}$
Maxwell-Boltzmann distribution	$P_{\text{MB}}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)$
Mean and RMS speeds	$\langle v \rangle = \left(\frac{8k_B T}{\pi m}\right)^{1/2} \quad \langle v^2 \rangle^{1/2} = \left(\frac{3k_B T}{m}\right)^{1/2}$
Pressure	$\langle P \rangle = \frac{\Delta p}{\Delta t} = m \frac{N}{V} \frac{1}{3} \langle v^2 \rangle = \frac{N k_B T}{V} = \frac{n R T}{V}$
Wall collision frequency	$J_W = \frac{1}{4} \frac{N}{V} \langle v \rangle = \frac{P}{(2\pi m k_B T)^{1/2}}$
Molecular collision frequency	$z = \sqrt{2} \sigma \langle v \rangle \frac{N}{V} = \frac{4\sigma P}{(\pi m k_B T)^{1/2}}$
Total collisions	$z_{AA} = \frac{1}{2} \frac{N}{V} z$
Mean free path	$\lambda = \frac{\langle v \rangle}{z} = \frac{V}{\sqrt{2} \sigma N}$
Graham's effusion law	$\frac{dN}{dt} = \text{Area} \cdot J_w \propto 1/m^{1/2}$
Effusion from a vessel	$P = P_0 e^{-t/\tau}, \tau = \frac{V}{A} \left(\frac{2\pi m}{k_B T}\right)^{1/2}$
Self-diffusion constant	$D_{11} = \frac{1}{3} \langle v \rangle \lambda$
Diffusion rate	$\langle x^2 \rangle^{1/2} = \sqrt{2Dt} \quad \langle r^2 \rangle^{1/2} = \sqrt{6Dt}$
Einstein-Smoluchowski equation	$D_{11} = \frac{\delta^2}{2\tau}$
Stokes-Einstein equation for liquids	$D_{11} = \frac{k_B T}{4\pi\eta r}$ "Slip" boundary
	$D_{\text{Brownian}} = \frac{k_B T}{6\pi\eta r}$ "Stick" boundary

1.4 Lecture 3: Transport

1. Effusion and Graham's law, effusion rate $\propto MW^{-1/2}$
2. Fick's first law: net flux proportional to concentration gradient
 - (a) $j_x = -D \frac{dc}{dx}$
 - (b) Self-diffusion constant, $D = \frac{1}{3} \lambda \langle v \rangle$
3. Knudsen diffusion, $D = \frac{1}{3} l \langle v \rangle$
4. Fick's second law: time evolution of concentration gradient
 - (a) Continuity with no advection: $\frac{\partial c}{\partial t} = -\nabla \cdot \vec{j} + \text{gen}$
 - (b) One-dimension: $\frac{dc}{dt} = D \frac{d^2 c}{dx^2}$
 - (c) Diffusion has Gaussian probability distribution: $c(x, t)/c_0 = [2\sqrt{\pi Dt}]^{-1} \exp(-x^2/4Dt)$
5. Seeing is believing—Brownian motion
 - (a) Seemingly random motion of large particles (“dust”) due to “kicks” from invisible molecules
 - (b) Einstein receives Nobel Prize for showing:
 - i. Motion follows same Gaussian diffusion behavior
 - ii. From steady-state arguments in a field, diffusion constant is ratio of Boltzmann energy, $k_B T$, to mobility
 - iii. Mobility inversely related to viscosity
 - (c) Stokes-Einstein equation
 - (d) Allows measurement of Avogadro's number, final proof of kinetic theory
 - (e) Similar model for diffusion of liquid molecules, slip boundary
6. Random walk model of diffusion
 - (a) Binomial distribution
 - (b) Large N and Stirling approximation
 - (c) Einstein-Smoluchowski relation

2 Quantum Mechanics: Blurred Lines Between Particles and Waves

2.1 Lecture 4: Duality and demise of classical physics

2.1.1 Properties of waves

1. traveling waves, $\psi(x, t) = A \sin(kx - \omega t)$, $k = 2\pi/\lambda$, $\omega = 2\pi\nu$
2. standing waves, $\psi(x, t) = A \sin(kx) \cos(\omega t)$
3. interference, diffraction
4. energy proportional to amplitude squared
5. Expected energy of a classical oscillator, $\langle \epsilon \rangle_\nu = k_B T$ for all ν

2.1.2 Blackbody radiation

1. Hohlraum spectrum
2. Stefan-Boltzmann law, total irradiance
3. Wien's displacement law
4. Rayleigh-Jeans and ultraviolet catastrophe
5. Planck model
 - (a) Energy spectrum of oscillators are *quantized*, $\epsilon_\nu = nh\nu$
 - (b) Expected energy of a quantized oscillator, $\langle \epsilon \rangle_\nu = h\nu / (e^{h\nu/k_B T} - 1)$
 - (c) Planck expression for blackbody radiation works!

```

1  import numpy as np
2  import matplotlib.pyplot as plt
3
4  hc = 1239.8          eV nm
5  c = 2.9979e8 * 1.e9  nm/s
6  k = 8.61734e5       eV /K
7  hck = hc/k          nm K
8
9  def Irrad(wl,T):
10     return (8. * np.pi * hc * c * wl**5) / (np.exp(hck/(wl*T))1)
11  def PlanckEnergy(wl,T):
12     return (hc/wl) / (np.exp(hck/(wl*T))1)
13
14  plt.figure()
15  wl=np.linspace(100,5000,1000)
16  for T in [1000.,2000.,3000.,4000.,5000.]:
17     Intensity = Irrad(wl,T)
18     plt.plot(wl,Intensity,label= K.format(T))
19
20  legend=plt.legend()
21  plt.xlabel(Wavelength (nm))
22  plt.ylabel(Irradiance (eV/nm3/s))
23  plt.title(Boltzmann distribution at various temperatures)
24  plt.savefig(./Images/BlackBody.png)
25
26  plt.figure()
27  color=[red,orange,green,blue,violet]
28  wl=np.linspace(100,20000,1000)
29  for T in [1000.,2000.,3000.,4000.,5000.]:
30     Energy = PlanckEnergy(wl,T)
31     plt.plot(wl,Energy,label= K.format(T),color=color[0])
32     kT = k*T
33     plt.plot([100,max(wl)], [kT,kT],ls=,color=color.pop(0))
34
35  legend=plt.legend()
36  plt.xlabel(Wavelength (nm))
37  plt.ylabel(Energy (eV))
38  plt.title(Boltzmann distribution at various temperatures)
39  plt.savefig(./Images/Planck.png)

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3 Statistical Mechanics: The Bridge from the Tiny to the Many

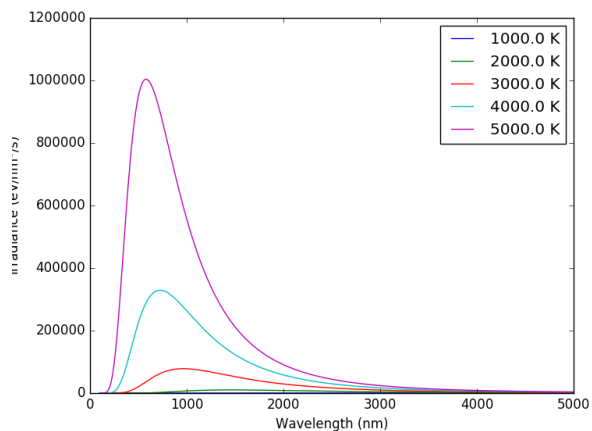


Figure 5: Blackbody irradiance

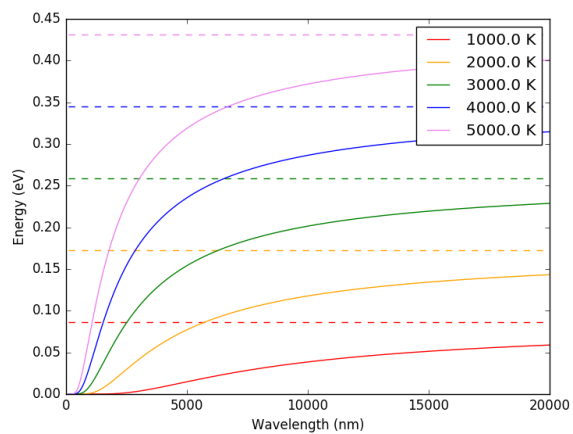


Figure 6: Average energy of a Planck quantized oscillator

Table 5: The new physics

Stefan-Boltzmann Law	$\int I(\lambda, T) d\lambda = \sigma_{\text{SB}} T^4$
Wien's Law	$\lambda_{\text{max}} T = 2897768 \text{ nm K}$
Rayleigh-Jeans eq	$I(\lambda, T) = \frac{8\pi}{\lambda^4} k_B T c$
Blackbody irradiance	$I(\lambda, T) = \frac{8\pi}{\lambda^5} \frac{hc^2}{e^{hc/\lambda k_B T} - 1}$
Einstein crystal	$C_v = 3R \left(\frac{h\nu}{k_B T} \right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2}$
Photon energy	$\epsilon = h\nu$
Rydberg equation	$\nu = R_H c \left(1/n^2 - 1/k^2 \right)$
Bohr equations	$l_n = n\hbar$
$n = 1, 2, \dots$	$r_n = n^2 \left(\frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} \right) = n^2 a_0$
	$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{1}{n^2} = -\frac{E_H}{2} \frac{1}{n^2}$
	$p_n = \frac{e^2}{4\pi\epsilon_0} \frac{m_e}{\hbar} \frac{1}{n} = p_0 \frac{1}{n}$
de Broglie equation	$\lambda = h/p$