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	J K^{-1} mol^{-1}	8.2057×10^{-2}	l atm mol^{-1} K^{-1}
σ_{SB}:	5.6704×10^{-8}	J s^{-1} m^{-2} 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}	C^2 J^{-1} m^{-1}	5.52635×10^{-3}	e^2 Å^{-1} eV^{-1}
$e^2/4\pi\epsilon_0$:	2.30708×10^{-28}	J m	14.39964	eV Å
a_0:	0.529177×10^{-10}	m	0.529177	Å
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) $P(E) \propto e^{-E/k_BT}$, in some sense the definition of temperature
   (b) Energy and its units
   (c) Absolute temperature and its units
   (d) k_BT 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, $P = P_0 e^{-mgh/k_BT}$
   (f) Kinetic energy in 1-D example
      i. $KE = \frac{1}{2}mv_x^2$
      ii. $P_{1D}(v_x) = \left(\frac{m}{2\pi k_BT}\right)^{1/2}\exp\left(-\frac{m|v_x|^2}{2k_BT}\right)$
      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, $\mu = \langle v_x\rangle = 0$, $\sigma^2 = \langle v_x^2\rangle = k_BT/m$
      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_BT	0.026 eV	0.026 eV
mgh/k_BT	2.4×10^{24}	2.3×10^{-5}
$P(1\,\text{m})/P(0)$	$e^{-2.4\times10^{-24}}$	0.99998
$\langle h\rangle$	0 m	42 km
$\langle v_x\rangle^{1/2}$	2×10^{-12} m/s	640 m/s

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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

```
import numpy as np
import matplotlib.pyplot as plt

R0 = 8.31441e3    kJ/mol K

def Boltzmann(E,T):
    return np.exp(E/(R0*T))/(R0*T)

energy = np.linspace(0,25,50)

plt.figure()
for Temperature in [100,300,1000]:
   Probability = Boltzmann(energy,Temperature)
   plt.plot(Probability,energy,label=0 K.format(Temperature))

legend = plt.legend()

plt.xlabel(Energy (kJ/mol))
plt.ylabel(Probability (mol/kJ))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/Boltzmann.png)

R0 = 8.31441    J/mol K
mass = 28./1000.    kg/mol
def MB1D(v,T):
    return np.sqrt(mass/(2*np.pi*R0*T))*np.exp((mass*v*v)/(2*R0*T))

velocity = np.linspace(1000,1000,1000)
plt.figure()
for Temperature in [100,200,300,400,500]:
    Probability = MB1D(velocity,Temperature)
    plt.plot(velocity,Probability,label= K.format(Temperature))

legend=plt.legend()
plt.xlabel(Velocity (m/s))
plt.ylabel(Probability (1/(m/s)))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/MB1D.png)
```

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 $<<$ total volume
2. Maxwell-Boltzmann distribution of molecular speeds

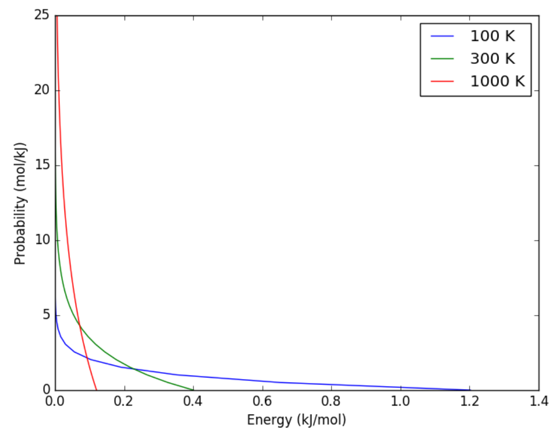

Figure 1: Boltzmann distribution at various temperatures

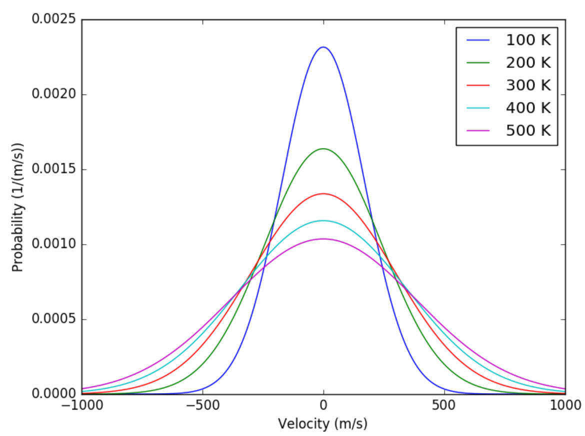

Figure 2: One-dimensional (Gaussian) velocities of N_2 gas

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

```
import numpy as np
import matplotlib.pyplot as plt

R0 = 8.31441    J/mol K
mass = 28. /1000  kg/mol N2

def Boltzmann(E,T):
    return np.exp(E/(R0*T))/(R0*T)

def MB(c,T):
    K = 0.5 * mass * c *c
    degeneracy = 4 * np.pi * c * c
    normalization = (mass/(2*np.pi*R0*T))**1.5
    return normalization*degeneracy*Boltzmann(K,T)

energy = np.linspace(0,1500,1500)

plt.figure()
for Temperature in [100,300,1000]:
   Probability = Boltzmann(energy,Temperature)
   plt.plot(Probability,energy,label=0 K.format(Temperature))

legend = plt.legend()

plt.xlabel(Energy (kJ/mol))
plt.ylabel(Probability (mol/kJ))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/Boltzmann.png)

R0 = 8.31441    J/mol K
mass = 28./1000.    kg/mol
def MB1D(v,T):
    return np.sqrt(mass/(2*np.pi*R0*T))*np.exp((mass*v*v)/(2*R0*T))

velocity = np.linspace(1000,1000,1000)
plt.figure()
for Temperature in [100,200,300,400,500]:
    Probability = MB1D(velocity,Temperature)
    plt.plot(velocity,Probability,label= K.format(Temperature))

legend=plt.legend()
plt.xlabel(Velocity (m/s))
```

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```
plt.ylabel(Probability (1/(m/s)))
 plt.title(Boltzmann distribution at various temperatures)
plt.savefig(./Images/MB1D.png)
```

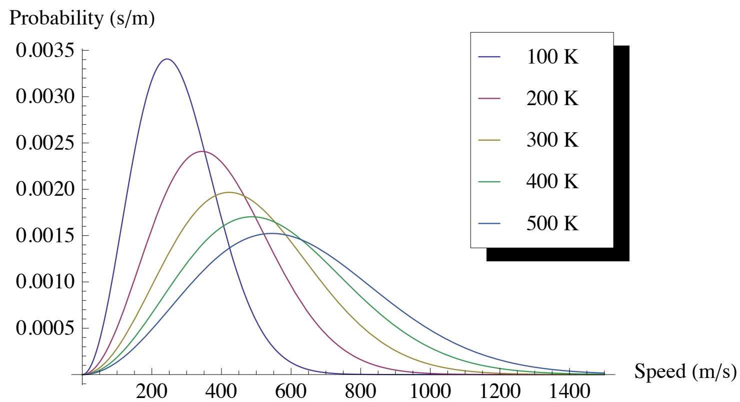

Figure 3: Maxwell-Boltzmann speed distribution of N_2 gas

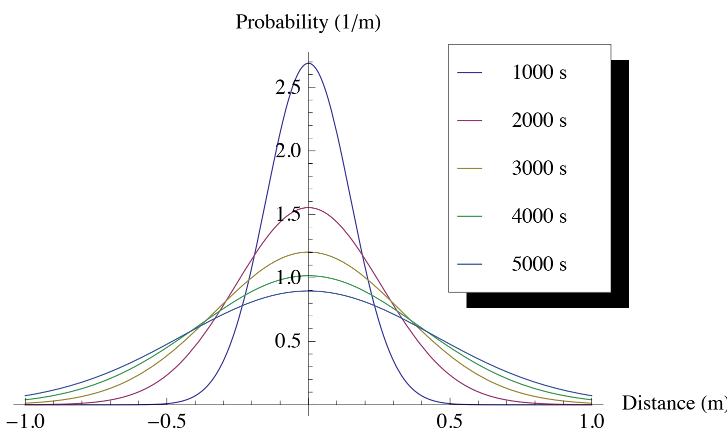

Figure 4: Diffusional spreading, $\sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$

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: $\frac{\partial c}{\partial t} = -\nabla \cdot \vec{j} + \text{gen}$

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Table 4: Kinetic theory of gases key equations

Boltzmann distribution ($g(E)$: degeneracy of E)	$P(E) = g(E)e^{-E/k_BT}$
Maxwell-Boltzmann distribution	$P_{\text{MB}}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_BT}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_BT}\right)$
Mean and RMS speeds	$\langle v\rangle = \left(\frac{8k_BT}{\pi m}\right)^{1/2} \quad \langle v^2\rangle^{1/2} = \left(\frac{3k_BT}{m}\right)^{1/2}$
Pressure	$\langle P\rangle = \frac{\Delta p}{\Delta t} = m\frac{N}{V}\frac{1}{3}\langle v^2\rangle = \frac{Nk_BT}{V} = \frac{nRT}{V}$
Wall collision frequency	$J_W = \frac{1}{4}\frac{N}{V}\langle v\rangle = \frac{P}{(2\pi mk_BT)^{1/2}}$
Molecular collision frequency	$z = \sqrt{2}\sigma\langle v\rangle\frac{N}{V} = \frac{4\sigma P}{(\pi mk_BT)^{1/2}}$
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	$P = P_0e^{-t/\tau}, \tau = \frac{V}{A}\left(\frac{2\pi m}{k_BT}\right)^{1/2}$
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	$D_{11} = \frac{k_BT}{4\pi\eta r}$ "Slip" boundary
	$D_{\text{Brownian}} = \frac{k_BT}{6\pi\eta r}$ "Stick" boundary

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(b) One-dimension: $\frac{dc}{dt} = D\frac{d^2c}{dx^2}$

(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_BT, 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

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

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