



UNIVERSITY OF
NOTRE DAME

Physical Chemistry for Chemical Engineers
(CHE 30324)

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NAME (PRINT): _____

NETID (PRINT): _____

*AS A MEMBER OF THE NOTRE DAME COMMUNITY, I WILL NOT
PARTICIPATE IN OR TOLERATE ACADEMIC DISHONESTY*

SIGNED: _____

WRITE YOUR SOLUTIONS IN THE SPACE INDICATED, MAKING SURE
YOUR APPROACH IS CLEAR. USE THE BACK OF THE TABLES PAGES
IF YOU NEED ADDITIONAL SCRATCH SPACE. WRITE YOUR NETID IN
THE UPPER RIGHT OF EACH PAGE.

1 Up in the air (40 pts)

Some potentially useful integral relationships:

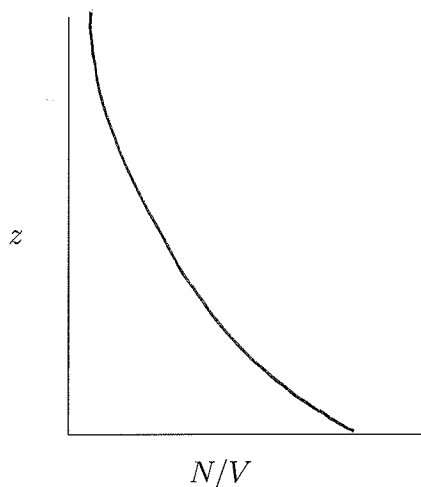
$$\int e^{-ax} dx = -e^{-ax}/a \quad \int xe^{-ax} dx = -(1+ax)e^{-ax}/a^2$$

The Boltzmann distribution describes how energy is distributed amongst available energy states at thermal equilibrium. For example, if the potential energy of a gas molecule a distance z above the surface of the earth is $U(z) = mgz$, where m is the object's mass and $g = 9.8 \text{ m s}^{-2}$ is the acceleration due to gravity, then the Boltzmann distribution tells us the vertical distribution of those molecules in the atmosphere at a given temperature.

- 1.1 (10 pts) Assuming the temperature of a column of air in the atmosphere is a constant T , write an expression for the relative probability of a molecule of mass m to be a distance z above the surface of the earth. No need to normalize.

$$\frac{P(z)}{P(0)} = \frac{e^{-mgz/k_B T}}{e^{-0/k_B T}} = e^{-mgz/k_B T}$$

- 1.2 (10 pts) Based on your answer, sketch the expected number density N/V of gas molecules of mass m vs distance z (altitude) above the earth's surface.



- 1.3 (8 pts) Calculate the ratio of the number density of CO_2 molecules (mass 44 amu) at an altitude of 11 km (about the altitude that a commercial airliner flies) to that at the earth's surface, assuming a constant $T = 25^\circ\text{C}$.

$$\frac{0.044 \frac{\text{kg}}{\text{mol}} \cdot 9.8 \text{ m/s}^2 \cdot 11 \times 10^3 \text{ m}}{8.314 \text{ J/mol} \cdot \text{K} \cdot 298 \text{ K}} = 1.914$$

$$e^{-1.914} = 0.147$$

- 1.4 (12 pts) Calculate the expectation value of the altitude of a CO_2 molecule at 25°C .

$$\langle z \rangle = \frac{\int_0^\infty z e^{-mgz/k_B T} dz}{\int_0^\infty e^{-mgz/k_B T} dz} = \frac{-(1+az)e^{-az}/a \Big|_0^\infty}{-e^{-az}/a \Big|_0^\infty}$$

use formulas w/ $a = \frac{mg}{k_B T}$

$$= 1.74 \times 10^{-4} \text{ m}^{-1}$$

$$= \frac{1+az}{a}$$

$$= \frac{0 - -1/a^2}{0 - -1/a}$$

$$= 1/a$$

$$= 5746 \text{ m}$$

2 Separating the big ones from the little ones (30 pts)

Uranium comes in primarily two isotopes, ^{238}U , natural abundance about 99.3%, and ^{235}U , natural abundance about 0.7%. The ^{235}U isotope has the shorter half-life and is the useful one for nuclear reactors (and bombs!). Uranium is "enriched" by selectively increasing the proportion of the ^{235}U isotope.

- 2.1 (10 pts) One way to enrich a mixture of uranium isotopes is by taking advantage of the different rates of effusion of gaseous $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$. If a vessel is filled with a mixture of these two gases in their natural proportions at 50°C , what is the ratio $^{235}\text{UF}_6/^{238}\text{UF}_6$ of gases exiting the vessel?

	Atomic mass (amu)
^{235}U	235
^{238}U	238
^{19}F (only isotope)	19

$$M_{235} = 235 + 6 \cdot 19 = 349$$

$$M_{238} = 238 + 6 \cdot 19 = 352$$

@ const T

$$\frac{Z_{w,235}}{Z_{w,238}} = \left(\frac{M_{238}}{M_{235}} \right)^{1/2} = \left(\frac{352}{349} \right)^{1/2} = 1.0042$$

$$\frac{^{235}\text{U}_{\text{Out}}}{^{238}\text{U}_{\text{Out}}} = 1.0042 \cdot \frac{^{235}\text{U}_{\text{In}}}{^{238}\text{U}_{\text{In}}} = 1.0042 \cdot \frac{0.007}{0.993} = \frac{0.0071}{1}$$

- 2.2 (5 pts) How would increasing the temperature of the vessel at constant volume affect the **proportion** of exiting gases?

Increase _____ Decrease _____ No change X

- 2.3 (5 pts) How would increasing the temperature of the vessel at constant volume affect the **rate** gases exit the vessel?

Increase X Decrease _____ No change _____

- 2.4 (10 pts) How many such effusion devices would have to be connected in series to increase the fraction of ^{235}U to 3%, about that used in a commercial nuclear power plant?

$$\frac{{}^{235}\text{Out}}{{}^{238}\text{Out}} = \frac{{}^{235}\text{In}}{{}^{238}\text{In}} \cdot (1.0042)^n = \frac{0.03}{0.97}$$

$$\frac{0.007}{0.993} \cdot (1.0042)^n = \frac{0.03}{0.97}$$

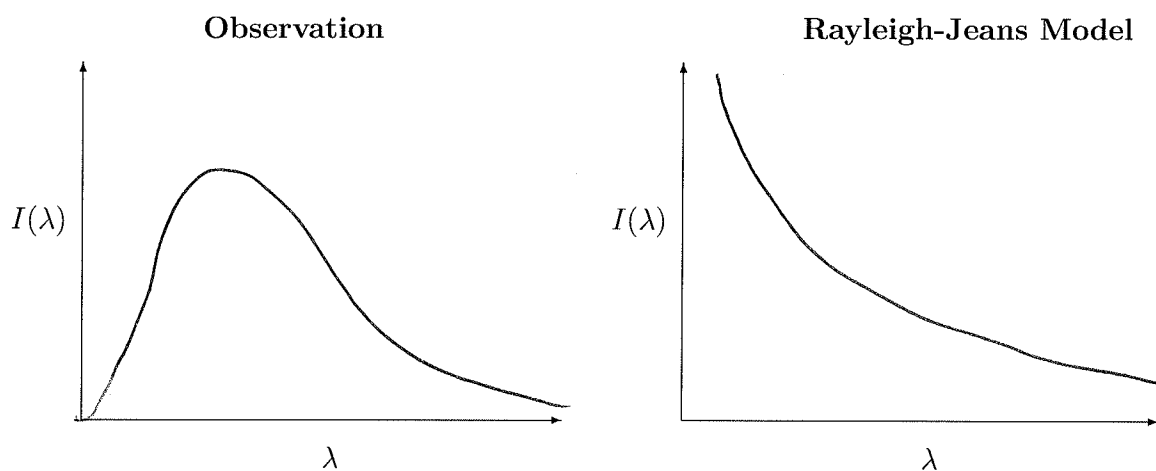
$$(1.0042)^n = 4.387$$

$$n \ln 1.0042 = \ln 4.387$$

$$n = \frac{\ln 4.387}{\ln 1.0042} \approx 353$$

3 It's raining photons (30 pts)

- 3.1 (10 pts) On the graph on the left below, provide a rough sketch of the spectrum of an ideal blackbody radiator. On the right, provide a rough sketch of what Rayleigh-Jeans models says it should look like.



- 3.2 (6 pts) What two things about the light in the blackbody radiator did Planck have to assume to explain the blackbody spectrum?

1. Thing 1: energy of light/oscillators is
 $\propto \nu$

2. Thing 2: energy takes only discrete values
 $E = m h \nu \quad m = 0, 1, 2, \dots$

- 3.3 (10 pts) The earth's surface receives about 340 W m^{-2} of energy from the sun, averaged over the planet's rotation and orbit. What would the equilibrium temperature of the earth's surface be if it behaved as a perfect blackbody radiator and re-emitted all this incoming energy?

Stefan - Boltzmann

$$I = \sigma_{SB} T^4$$

$$T = \left(\frac{I}{\sigma_{SB}} \right)^{1/4}$$

$$= \left(\frac{340 \text{ W/m}^2}{5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4} \right)^{1/4}$$

$$= 278 \text{ K}$$

$$= 5^\circ \text{C}$$

$$= 41^\circ \text{F}$$

- 3.4 (4 pts) Very briefly, why is the earth warmer than your answer?

greenhouse effect

earth receives radiation in spectral region that atmosphere is transparent, emits in region that atmosphere is not.

4 Tables

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}	$\text{e}^2 \text{\AA}^{-1} \text{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	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

Table 2: 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

Table 3: 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	$P_{MB}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left(-\frac{mv^2}{2k_B T} \right)$
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	$\langle P \rangle = \frac{\Delta p}{\Delta t} = m \frac{N}{V} \frac{1}{3} \langle v^2 \rangle = \frac{Nk_B T}{V} = \frac{nRT}{V}$
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

Table 4: Classical waves

The wave equation	$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2}$
General solution	$\Psi(x, t) = A \sin(kx - \omega t)$
Wavelength (distance)	$\lambda = 2\pi/k$
Frequency (/time)	$\nu = \omega/2\pi$
Speed	$v = \lambda\nu$
Amplitude (distance)	A
Energy	$E \propto A^2$
Standing wave	$\Psi(x, t) = A \sin(kx) \cos(\omega t), \quad k = n\pi/a$

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	$l_n = n\hbar$
$n = 1, 2, \dots$	$r_n = n^2 \left(\frac{4\pi\epsilon_0 \hbar^2}{e^2 m_e} \right) = n^2 a_0$
	$E_n = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2} = -\frac{E_H}{2} \frac{1}{n^2}$
	$p_n = \frac{e^2}{4\pi\epsilon_0} \frac{m_e}{\hbar} \frac{1}{n} = p_0 \frac{1}{n}$
de Broglie equation	$\lambda = h/p$