Physical Chemistry for Chemical Engineers (CHE 30324)

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NAME (PRINT):____

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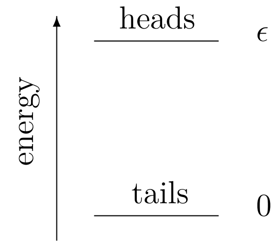
SIGNED: ____

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 Two states. We want two states. (30 pts)

A normal coin lands on heads or tails with equal probability. Imagine a coin that is higher in energy by some amount ϵ if it lands on heads rather than tails:



1.1 (10 pts) Write down the normalized Boltzmann probability for this imaginary coin to land on tails if it is flipped at some temperature T.

$$\tilde{P}_{tail} = \frac{e^{-\varepsilon_{tail}/k_B T}}{\sum e^{-\varepsilon/k_B T}} \quad 5 \quad = \frac{e^{-0}}{1 + e^{-\varepsilon/k_B T}}$$

$$= \frac{1}{1 + e^{-\varepsilon/k_B T}} \quad 5$$

1.2 (10 pts) What is the expectation value of the number of tails in 100 of these coins tossed at a temperature $T = \epsilon/k_B$?

$$\tilde{P}_{tail} = \frac{1}{1 + e^{-1}} \quad 5 \quad = \frac{1}{1+e^{-1}} \approx 0.73 \quad 3$$

$$\langle tail \rangle = 100 \cdot 0.73 = 73$$

2

1.3 (10 pts) What is the expectation value of the total energy of 100 coins tossed at a temperature $T = \epsilon/k_B$?

$$\langle \varepsilon \rangle = 100 \sum_{h,t} \varepsilon_i P_i$$ 6

$$= 100\,(0 \cdot 0.73 + \varepsilon \cdot 0.27)$$

$$= 27\varepsilon$$ 4

2 Full of nothing. (30 pts)

Ultrahigh vacuum (UHV) chambers are frequently used to study the interactions of gases with surfaces. UHV is defined as $\approx 10^{-7}$ Pa, and a typical UHV chamber is a cube about 10 cm on a side. Let's assume the residual gas within the chamber is N_2 (MW of 0.028 kg mol^{-1}) and is at 300 K, so $RT = 2500\,\mathrm{Pa\,m^3\,mol^{-1}}$.

2.1 (5 pts) About how many N_2 molecules are in the UHV chamber?

$$N = V\left(\frac{P}{RT}\right) = (0.1\,m)^3\left(\frac{10^{-7}\,Pa}{2500\,Pa\,m^3/mol}\right)$$ 4

$$= 4\times10^{-14}\,mol$$

$$= 2\times10^{10}\text{ molecules}$$ 1

2.2 (5 pts) If N_2 has a collision cross section of 0.4 nm^2, about how many collisions does one starting at the center of the chamber make before hitting the chamber wall? (*Hint*: Consider the mean free path.)

$$\lambda = \frac{1}{\sqrt{2}\left(\frac{N}{V}\right)\cdot\sigma} = \frac{1}{\sqrt{2}\left(\frac{P}{RT}\right)\sigma}$$

$$= \frac{1}{\sqrt{2}}\left(\frac{2500\,Pa\,m^3/mol}{10^{-7}\,Pa}\right)\cdot\frac{1}{0.4\times10^{-18}\,m^2}\cdot\frac{1}{N_{av}}$$

$$= 7\times10^{4}\,m \gg \text{chamber size}$$ 3

2 0 collisions before hitting wall

2.3 (5 pts) Is it reasonable to describe the gas molecules in the chamber as diffusing by a random walk process? Why or why not?

no. No molecule-molecule collisions.

3 2

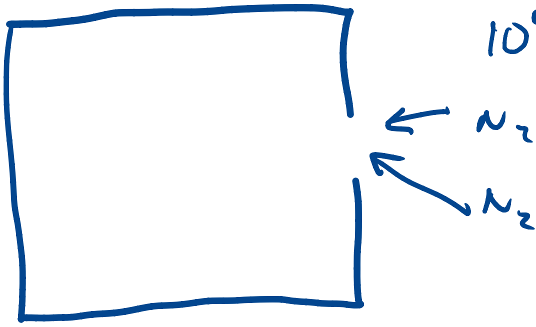
2.4 (5 pts) What is the mean speed ($\langle v \rangle$) of an N_2 molecule inside the UHV chamber?

$$\langle v \rangle = \left(\frac{8RT}{\pi \cdot MW} \right)^{1/2} = \left(\frac{8 \cdot 2500 \text{ Pa m}^3/\text{mol}}{\pi \cdot 0.028 \text{ kg/mol}} \right)$$

$$= 480 \text{ m/s}$$

5

2.5 (10 pts) Suppose the UHV chamber has a pinhole one micrometer in diameter (an area of about 10^{-12} m) and your lab is also full of N_2 at 300 K and 1 bar (10^5 Pa). About how long will it take for the pressure inside the chamber to rise to 10^{-5} Pa?



10^5 Pa

$$N_{box} = \left(\frac{P}{RT}\right)\cdot V$$

4

$$= \left(\frac{10^{-5}\ \text{Pa}}{2500\ \text{Pa m}^3/\text{mol}}\right)\cdot(0.1\,\text{m})^3$$

$$= 4\times10^{-12}\ \text{mol}$$

$$\frac{dN_{box}}{dt} = \text{in} - \cancelto{\approx 0}{\text{out}} + \cancelto{0}{\text{gen}} - \cancelto{0}{\text{consump}}$$

$$= J_w\cdot A = \text{constant}$$

4

$$= \frac{1}{4}\left(\frac{N}{V}\right)\langle v\rangle\cdot A$$

$$= \frac{1}{4}\left(\frac{P}{RT}\right)\langle v\rangle\cdot A$$

$$= \frac{1}{4}\left(\frac{10^5\ \text{Pa}}{2500\ \text{Pa m}^3/\text{mol}}\right)\cdot 480\,\text{m/s}\cdot 10^{-12}\,\text{m}^2$$

$$= 4.8\times10^{-9}\ \text{mol/s}$$

$$t = \frac{4\times10^{-12}\ \text{mol}}{4.8\times10^{-9}\ \text{mol/s}} = 8\times10^{-4}\ \text{s}$$

2

3 Disappointing. Sure. Catastrophic. That's a bit much. (40 pts)

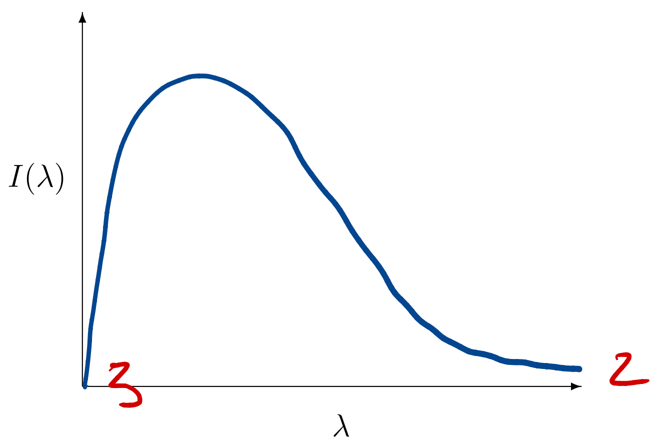
The "ultraviolet catastrophe" refers to the unphysical predictions the Rayleigh-Jeans model makes for the spectrum of light emitted by an ideal blackbody radiator.

3.1 (5 pts) In one word, what determines the spectrum of an ideal blackbody radiator?

temperature

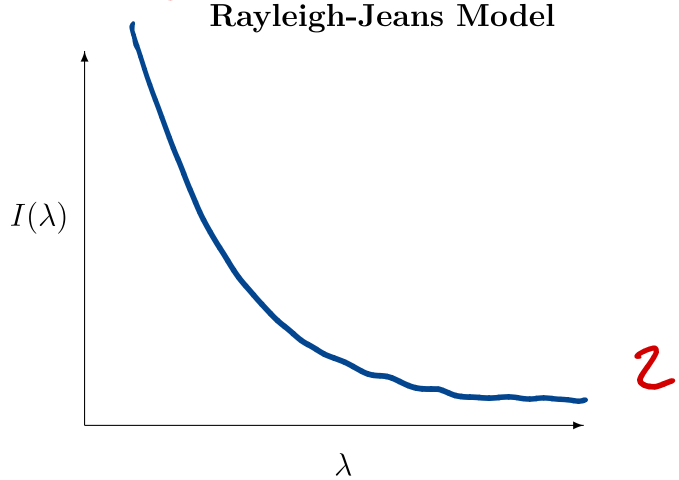
3.2 (10 pts) On the graph on the top below, provide a rough sketch of the spectrum of an ideal blackbody radiator. On the bottom, provide a rough sketch of what Rayleigh-Jeans models says it should look like.

Observation



3

Rayleigh-Jeans Model



3.3 (6 pts) Planck assumed that the blackbody radiator was full of quantized oscillators. Imagine a black body radiator at $T = 11\,600\,\mathrm{K}$, so that $k_B T = 1\,\mathrm{eV}$. What is the ratio of the probability to have one vs zero quanta of energy in a $12\,400\,\mathrm{nm}$ oscillator?

$$\varepsilon = nh\nu = nhc/\lambda$$

$$\frac{P_{n=1}}{P_{n=0}} = \frac{e^{-hc/\lambda kT}}{e^0} = e^{-1240\,\mathrm{eV\text{-}nm}/1\,\mathrm{eV}\cdot 12400\,\mathrm{nm}}$$

4

$$= e^{-0.1}$$

$$= 0.9$$

2

3.4 (4 pts) Imagine the same black body radiator at $T = 11\,600\,\mathrm{K}$, so that $k_B T = 1\,\mathrm{eV}$. What is the ratio of the probability to have one vs zero quanta of energy in a $1.24\,\mathrm{nm}$ oscillator?

$$\frac{P_{n=1}}{P_{n=0}} = \frac{e^{-hc/\lambda kT}}{e^0} = e^{-1240\,\mathrm{eV\text{-}nm}/1\,\mathrm{eV}\cdot 1.24\,\mathrm{nm}}$$

2

$$= e^{-1000}$$

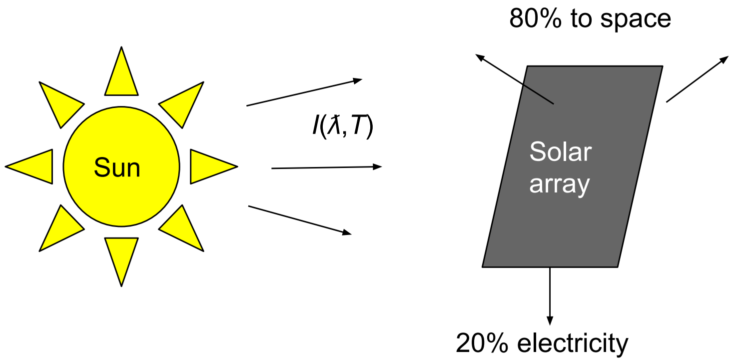
$$\sim 0$$

2

3.5 (2 pts) Why, briefly, are these two answers different?

Boltzmann dist – lower probability to be in a high energy state

3.6 (13 pts) You are the radiation engineer at SpaceX, put on a project to put a solar array into space. The array is made from a large, thin sheet of dark material that absorbs and emits light like a blackbody radiator. When deployed, the array will receive $500\,\mathrm{W\,m^{-2}}$ from the sun. The array is 20% efficient, so that 20% of the incident radiation is converted into electricity and the rest is reemitted as blackbody radiation. What is the equilibrium temperature of the array? (Remember the array has two sides, but only one faces the sun!)



$$I_{out} = 500\,\frac{W}{m^2} * 0.8 * \frac{1}{2} = 200\,W/m^2$$ 8

$$= \sigma T^4$$

$$T = \left(\frac{I}{\sigma}\right)^{1/4} = \left(\frac{200\,W/m^2}{5.6\times10^{-8}}\right)^{1/4}$$ 5

$$= 244\,K$$

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}	$\mathrm{J\ K}^{-1}$	8.61734×10^{-5}	$\mathrm{eV\ K}^{-1}$
R:	8.314472	$\mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$	8.2057×10^{-2}	$\mathrm{l\ atm\ mol}^{-1}\ \mathrm{K}^{-1}$
σ_{SB}:	5.6704×10^{-8}	$\mathrm{J\ s}^{-1}\ \mathrm{m}^{-2}\ \mathrm{K}^{-4}$		
c:	2.99792458×10^{8}	$\mathrm{m\ s}^{-1}$		
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	$\mathrm{MeV\ c}^{-2}$
ϵ_0:	8.85419×10^{-12}	$\mathrm{C}^2\ \mathrm{J}^{-1}\ \mathrm{m}^{-1}$	5.52635×10^{-3}	$e^2\ \mathrm{Å}^{-1}\ \mathrm{eV}^{-1}$
$e^2/4\pi\epsilon_0$:	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

Table 2: Energy conversions and correspondences

	J	eV	Hartree	$\mathrm{kJ\ mol}^{-1}$	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 $\mathrm{kJ\ mol}^{-1}$ =	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)	$P(E) = g(E)e^{-E/k_BT}$
Maxwell-Boltzmann distribution	$P_{\mathrm{MB}}(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_BT}\right)$
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	$J_W = \frac{1}{4}\frac{N}{V}\langle v \rangle = \frac{P}{(2\pi m k_B T)^{1/2}}$
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	$P = P_0 e^{-t/\tau}, \tau = \frac{V}{A}\left(\frac{2\pi m}{k_BT}\right)^{1/2}$
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
	$D_{\mathrm{Brownian}} = \frac{k_BT}{6\pi\eta r}$ "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	$\int I(\lambda,T)d\lambda = \sigma_{\mathrm{SB}}T^4$
Wien's Law	$\lambda_{\max}T = 2897768$ nm K
Rayleigh-Jeans eq	$I(\lambda,T) = \frac{8\pi}{\lambda^4}k_BTc$
Blackbody irradiance	$I(\lambda,T) = \frac{8\pi}{\lambda^5}\frac{hc^2}{e^{hc/\lambda k_BT} - 1}$
Einstein crystal	$C_v = 3R\left(\frac{h\nu}{k_BT}\right)^2\frac{e^{h\nu/k_BT}}{\left(e^{h\nu/k_BT} - 1\right)^2}$
Photon energy	$\epsilon = h\nu$
Rydberg equation	$\nu = R_Hc\left(1/n^2 - 1/k^2\right)$
Bohr equations	$l_n = n\hbar$
$n = 1, 2, \ldots$	$r_n = n^2\left(\frac{4\pi\epsilon_0\hbar^2}{e^2m_e}\right) = n^2a_0$
	$E_n = -\frac{m_ee^4}{8\epsilon_0^2h^2}\frac{1}{n^2} = -\frac{E_H}{2}\frac{1}{n^2}$
	$p_n = \frac{e^2}{4\pi\epsilon_0}\frac{m_e}{\hbar}\frac{1}{n} = p_0\frac{1}{n}$
de Broglie equation	$\lambda = h/p$