Q1.	7
Q2.	7
Q3.	7
Q4.	7
Q5.	7
Q6.	8
Q7.	7
	50

This is a <u>**three-hour test**</u>.

Please answer all <u>**seven questions**</u> in the spaces provided.

A calculator and the equation sheets provided can be used.

No books or notes are allowed. No marks for unreadable answers.

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1. This question refers to a blackbody radiation source with the emissivity spectrum plotted below.

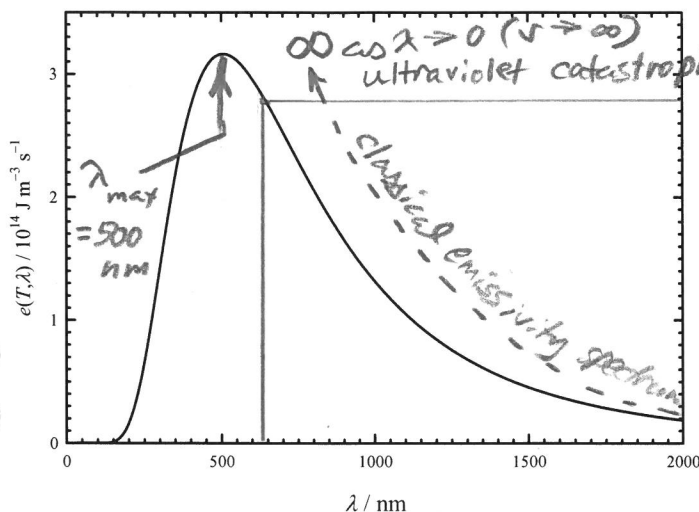**a)** On the diagram, sketch the emissivity spectrum predicted by classical physics.

$$e(T,r) \to \infty \quad \text{as} \quad r \to \infty$$
$$e(T,\lambda) \to \infty \quad \lambda \to 0$$

b) Use Wein's law $\lambda_{max} T = hc/4.965k$ to estimate the temperature of the blackbody.

$$T = \frac{hc}{4.965\,k\,\lambda_{max}}$$

$$= \frac{(6.626\times10^{-34})(2.998\times10^{8})}{4.965(1.381\times10^{-23})(500\times10^{-9})}$$

$$\boxed{T = 5800 \ K}$$

∞ as $\lambda \to 0$ $(r \to \infty)$
ultraviolet catastrophe!

classical emissivity spectrum

$\lambda_{max} = 500$ nm

y-axis: $e(T,\lambda) / 10^{14} \ J \ m^{-3} \ s^{-1}$
x-axis: λ / nm (0, 500, 1000, 1500, 2000)

c) Calculate the total emissivity of the blackbody.

[7]

$$\int_0^\infty e(T,\lambda)\,d\lambda = \sigma T^4 = (5.670\times10^{-8})(5800)^4$$

$$= \boxed{6.4\times10^{7} \ J \ m^{-2} \ s^{-1}}$$

d) Narrow-band filters are used to study radiation emitted at specific wavelengths. Use the diagram to calculate the emissivity of the blackbody **at wavelengths from 633 nm to 635 nm**.
(*note: lengthy numerical calculations are not required to answer this question*)

$$\int_{633nm}^{635nm} e(T,\lambda)\,d\lambda \cong e(T, 634\,nm)(2\,nm)$$

$$= (2.8\times10^{14} \ J\,m^{-3}\,s^{-1})(2\times10^{-9}\,m)$$

$$= \boxed{5.6\times10^{5} \ J \ m^{-2} \ s^{-1}} \quad (\sim 0.9\% \ \text{of tot. emiss.})$$

read from graph at $\lambda = 634$ nm

$$= \text{area of a rectangle of height } 2.8\times10^{14} \ J\,m^{-3}\,s^{-1}$$
$$\text{and width } 2\times10^{-9} \ m$$

2. a) Why is the zero point energy of a particle in a box non-classical?

The minimum energy the particle can have is $h^2/8mL^2$. Classically, a particle can have zero velocity and zero kinetic energy — not possible for a confined quantum particle.

b) For a 2.7-gram ping pong ball in a 50.0-cm-wide box:

(0.0027 kg)   (0.500 m)

i) Calculate the zero point energy ($E_1 = h^2/8mL^2$).

$$E_1 = \frac{(6.626 \times 10^{-34})^2}{8(0.0027)(0.500)^2}$$

$$= \boxed{8.13 \times 10^{-65} \text{ J}} \quad \left(5.07 \times 10^{-46} \text{ eV}\right)$$

ii) Is the value of E_1 significant? Justify your answer.

[7]   No. E_1 is completely neglible compared to $kT/2$, the average thermal energy of a particle (2×10^{-21} J at room temperature)

c) For an electron in a 0.10-nm-wide box:

i) Calculate the zero point energy.

$$E_1 = \frac{(6.626 \times 10^{-34})^2}{8(9.110 \times 10^{-31})(0.10 \times 10^{-9})^2} = \boxed{6.02 \times 10^{-18} \text{ J}}$$
$$(37.5 \text{ eV})$$

ii) Calculate the de Broglie wavelength $\lambda = h/p$.

$$E_1 \left(\text{all kinetic}\right) = \frac{mv^2}{2} = \frac{m^2 v^2}{2m} = \frac{p^2}{2m}$$

momentum $p = \sqrt{2mE_1}$

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE_1}} = \frac{h}{\sqrt{\frac{2m h^2}{8mL^2}}} = \frac{1}{\sqrt{\frac{1}{4L^2}}} = 2L$$

$$\boxed{\lambda = 0.20 \text{ nm}}$$

iii) Are the values of E_1 and λ significant? Justify your answer.

Yes. E_1 is 3000 times larger than $kT/2$ and about 3 times larger than the ground state energy of the H atom (-13.6 eV). λ is twice as large as the box.

d) Use the results from this question to explain why chemists need to use quantum mechanics (not classical mechanics) to understand the properties of atoms and molecules.

Electrons behave as waves (not particles) on atomic and molecular scales.

3. This question refers to the harmonic oscillation of mass m with frequency v and force constant k.

    Data: $m = 0.050$ kg $v = 1.2$ s^{-1} oscillation amplitude: $A = 0.035$ m

          force constant $k = 2.84$ N m^{-1} displacement at time t: $x(t) = A\cos(2\pi vt)$

a) The potential energy of the oscillator is $V(t) = kx(t)^2/2$. Use the general result that force equals the negative gradient of the potential energy to show the force acting on the mass is $-kx(t)$.

$$-\frac{\partial V}{\partial x} = -\frac{\partial}{\partial x}\frac{k\,x(t)^2}{2} = -\frac{k}{2}\frac{\partial\,x(t)^2}{\partial x} = -\frac{k}{2}\left(2x(t)\right)$$

$$= -k\,x(t)$$

b) Verify that $x(t) = A\cos(2\pi vt)$ is a valid solution of Newton's law of motion $(F = ma)$

$$-kx(t) = m\frac{d^2 x(t)}{dt^2}$$

and show $k = 4\pi^2 mv^2$.

$$RS = m\frac{d^2 x(t)}{dt^2} = m\frac{d}{dx}\frac{d}{dx}A\cos(2\pi vt)$$

$$= -m\frac{d}{dx}A(2\pi v)\sin(2\pi vt)$$

$$= -m\,A(2\pi v)(2\pi v)\cos(2\pi vt) = -m4\pi^2 v^2\,A\cos(2\pi vt)$$

[7]
$$= \underline{\underline{-m4\pi^2 v^2\,x(t)}} \qquad k = 4\pi^2 v^2$$

$$LS = \underline{\underline{-k\,x(t)}}$$

c) Calculate the kinetic energy of the oscillator at time $t = 110$ s.

$$\text{kinetic energy} = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{dx(t)}{dt}\right)^2$$

$$= \frac{1}{2}m\left(\frac{d}{dt}A\cos(2\pi vt)\right)^2 = \frac{1}{2}m\left(-A2\pi v\sin(2\pi vt)\right)^2$$

$$= \frac{1}{2}m\left(A2\pi v\,\sin\left[2\pi(1.2\,s^{-1})(110\,s)\right]\right)^2$$

$$= \frac{1}{2}m\left(A2\pi v\,\sin\left[2\pi(132)\right]\right)^2 = \boxed{0}$$

3

$$\frac{d^2}{dx^2}\sin(ax) = -a^2\sin(ax)$$

4. This question refers to a particle in a box between $x = 0$ and $x = L$ described by the wave function

$$\psi(x) = (2/L)^{1/2}\sin(\pi x/L)$$

a) Show $\psi(x)$ is an eigenfunction of the kinetic energy operator $-\dfrac{h^2}{8\pi^2 m}\dfrac{d^2}{dx^2}$ with eigenvalue $E = \dfrac{h^2}{8mL^2}$

$$\hat{T}\psi(x) = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\sqrt{\frac{2}{L}}\sin(\pi x/L)$$

$$= -\frac{h^2}{8\pi^2 m}\sqrt{\frac{2}{L}}\left(-\frac{\pi^2}{L^2}\right)\sin(\pi x/L)$$

$$= \frac{h^2}{8mL^2}\ \psi(x)$$

b) Show $\psi(x)$ is not an eigenfuction of the momentum operator $-\dfrac{ih}{2\pi}\dfrac{d}{dx}$. What are the implications of this result for measuring the momentum of the particle?

$$\hat{P}_x\psi(x) = -\frac{ih}{2\pi}\frac{d}{dx}\sqrt{\frac{2}{L}}\sin(\pi x/L)$$

$$= -\frac{ih}{2\pi}\sqrt{\frac{2}{L}}\frac{\pi}{L}\cos(\pi x/L) \neq \text{constant }\sin\left(\frac{\pi x}{L}\right)$$

[7]

$$\neq \text{constant }\psi(x)$$

$\psi(x)$ is not an eigenfunction of $\hat{P}_x$, P_x cannot be determined

c) Give the probability distribution function for the particle in the box and show it is normalized on the interval from $x = 0$ to $x = L$. Useful integral: $\int\sin^2(ax)dx = \dfrac{x}{2} - \dfrac{1}{4a}\sin(2ax)$

$$P(x) = \psi^*(x)\psi(x) = \psi(x)\psi(x) \quad \left(\text{because }\psi(x)\text{ is real: }\psi^*(x) = \psi(x)\right)$$

$$P(x) = \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)$$

$$\boxed{a = \pi/L}$$

$$\int_0^L P(x)dx = \int_0^L \frac{2}{L}\sin^2\left(\frac{\pi x}{L}\right)dx = \frac{2}{L}\left(\frac{x}{2} - \frac{\sin(2\pi x/L)}{2\pi/L}\right)\Bigg|_0^L$$

$$= \frac{2}{L}\left(\frac{L}{2} - \frac{\sin(2\pi)}{2\pi/L}^{\,0} - \frac{0}{2} + \frac{\sin(0)}{2\pi/L}^{\,0}\right)$$

$$= 1$$

4

5. a) i) According to classical physics, the kinetic energy of photoelectrons emitted by metals exposed to radiation should increase with the intensity of the radiation. Why?

higher intensity light waves have larger amplitude and more energy to knock out photoelectrons from metals

ii) Experiments show photoelectron kinetic energies increase with the frequency of the radiation (not with the radiation intensity). How did Einstein account for this result?

light (and other electromagnetic radiation) of frequency ν exists as photons of energy $h\nu$, not as classical waves of variable amplitude and energy

b) i) Give the key assumption made by Einstein to derive $U_m(T) = 3RT\dfrac{h\nu}{kT}\dfrac{1}{e^{h\nu/kT}-1}$ for the molar vibrational energy of a monatomic crystal.

the oscillating atoms have discrete energies $0, h\nu, 2h\nu, 3h\nu, \ldots$ (ν is the fundamental vibration frequency) not continuous energy $E \geq 0$

ii) Show $U_m(T) \to 0$ at low temperatures. Why is this result non-classical?

$$U_m(T) = 3RT \frac{y}{e^y - 1} \qquad (y \equiv h\nu/kT)$$

$$\lim_{\substack{T \to 0 \\ (y \to \infty)}} U_m(T) = \lim_{y \to \infty} 3RT \frac{y}{1 + y + \frac{y^2}{2} + \cdots - 1}$$

$$= \lim_{y \to \infty} 3RT \frac{1}{1 + \frac{y}{2} + \cdots}$$

$$= 0 \qquad \text{classically, } U_m(T) = 3RT \text{ (not zero)}$$

[7]

c) Prove $-3 + 4i$ is a solution of the quadratic equation $x^2 + 6x + 25 = 0$.

$$(-3 + 4i)^2 + 6(-3 + 4i) + 25$$
$$= 9 - 24i + 16i^2 - 18 + 24i + 25$$
$$= 9 + 16(-1) - 18 + 25$$
$$= 0$$

5
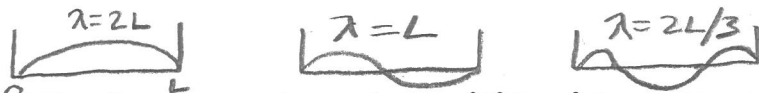
6. a) We used Shrodinger's equation to derive $n^2h^2/8mL^2$ for the kinetic energy of a quantum particle of mass m in a box of width L. *There's an easier way!*

i) The particle in the box has discrete (not continuous) wavelengths $2L$, L, $2L/3$, … Why?

to satisfy the boundary conditions for fitting waves in the box (no displacement at $x=0$ and $x=L$)
$\lambda = 2L, L, 2L/3 \ldots$ $\lambda = 2L/n$ $L = n\lambda/2$

ii) The result $\lambda_n = 2L/n$ $(n = 1, 2, 3, …)$ from **a** illustrates the origins of quantization. Explain.

only "discrete" (not continuous) waves of length $2L/n$ are "allowed", this means only discrete momenta are "allowed" ($P_x = h/\lambda$), which means only discrete energies $P_x^2/2m$

iii) Use de Broglie's relation $p_x = h/\lambda$ to show the particle momentum values are $\pm nh/2L$.

$$P_x = \frac{h}{\lambda} = \frac{h}{2L/n} = \frac{nh}{2L}$$

[8]

the particle can also be moving in the negative-x direction ($v_x < 0$), which gives $P_x = -\frac{nh}{2L}$

iv) Finally, use the allowed momentum values to show the kinetic energy of the particle is $n^2h^2/8mL^2$. *Hint:* $mv_x^2/2 = (mv_x)^2/2m = p_x^2/2m$

$$\text{kinetic energy} = \frac{P_x^2}{2m} = \frac{\left(\frac{nh}{2L}\right)^2}{2m} = \frac{n^2h^2}{8mL^2}$$

b) A quantum mechanical particle is described by the wave function $\psi(x) = Ae^{-i2\pi\nu t}$.

i) $\psi(x)$ is a complex function. What does "complex" mean in this context?

$\psi(x) = A(\cos(-2\pi\nu t) + i\sin(2\pi\nu t))$
      real part   imaginary part (proportional to $\sqrt{-1}$)

complex: real and imaginary components

ii) Give $\psi^*(x)$.

$Ae^{+i2\pi\nu t}$

iii) Show $\psi^*(x)\psi(x)$ is a real function.

$\psi^*(x)\psi(x) = Ae^{i2\pi\nu t} Ae^{-i2\pi\nu t} = A^2 e^{i2\pi\nu t - i2\pi\nu t} = A^2 e^0$
$= A^2$

iv) Why must $\psi^*(x)\psi(x)$ be a real function?

$\psi^*(x)\psi(x) = $ the probability distribution function $P(x)$
$P(x)$ and derived probabilities must be real numbers

6

7. **a)** A **pyrometer** is a remote-sensing device used to measure the temperature of objects without being in physical contact with the objects. How is this possible?

— blackbody radiation emissivity at temperature T is σT^4

— use a spectrophotometer to measure the emissivity (mostly IR at room temperature)

— calculate T

b) Pyrometer temperature measurements are unreliable for shiny objects. Why?

"Shiny" objects have lower emissivities than the assumed blackbody emissivity, and can reflect radiation emitted by other objects, giving false pyrometer temperature readings

[7]

c) **Arc welding** uses large electric currents to melt and join pieces of metal. Electric arc temperatures can reach 20,000 K. Give <u>two reasons</u> why arc welders must wear eye protection.

20,000 K is about 4 times hotter than the sun, which means electric arcs can be $4^4 = \underline{256 \text{ brighter than the sun.}}$
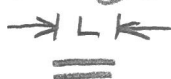
Also, $\lambda_{max} = 145\text{nm}$ in the <u>ultraviolet</u>, which can "burn" retinas (very bad)

d) Conjugated hydrocarbons (such as 1,3-butadiene and benzene) have lower energies than expected. Organic chemists "explain" to us that this behavior is caused by delocalization of π electrons.
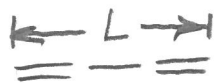
But why does delocalization lower the electron energies? Use particle-in-a-box theory to explain the reduction in electron energy caused by delocalization.

π electrons behave (approximately) as particles in molecular boxes. Delocalization means the electrons are in "bigger boxes", not confined to a single bond. The particle-in-a-box energy is inversely proportional to the square of the box size, so a larger box means lower π electron energies.

→ L ←   ← L → $E_{\pi \atop electron} \propto \frac{1}{L^2}$

ethylene   1,3-butadiene

Q1
Q2
Q3
Q4
Q5
Q6
Q7

7