

IMPERIAL COLLEGE LONDON

B.Eng., M.Eng and ACGI Examinations 2017
Part 1

Biomedical Engineering

BE1-HHMT1 Heat & Mass Transport 1

day, 00 Month 2016 00.00 -01.30pm

Duration: 1.5 hour

The paper has FOUR questions.

Answer ALL FOUR questions.

Marks for questions and parts of questions are shown next to the question. The marks for questions (and parts thereof) are indicative, and they may be slightly moderated at the discretion of the Examiner

Quadratic formula $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$0^\circ\text{C} = 273.15 \text{ K}$

Boltzmann's constant $k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1}$

Avagadro's number, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

The permittivity of free space is $8.85 \times 10^{-12} \text{ F m}^{-1}$

The Stefan-Boltzmann constant $5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$

The charge on an electron is $1.60 \times 10^{-19} \text{ C}$ or $9.647 \times 10^4 \text{ C mol}^{-1}$.

- 1 a) State the first two laws of thermodynamics.**
10 marks
- b) Calculate the work done on the system for the following cases:**
- (i) charging a 12.0 V battery for 2.00 hours at 5.00 A**
10 marks
- (ii) A 5.0 cm long piece of muscle is stretched longitudinally to 5.2 cm under load from a weight. The muscle follows Hooke's Law. A 300 N weight stretches the muscle from 5.0 cm to 5.1 cm.**
10 marks
- c) Give equations for Fourier's Law of heat transfer, Stefan-Boltzmann Law and Newton's law of cooling. State which mode of heat transfer is described, define the variables and units.**
15 marks
- d) Parylene C is a polymer which is widely used to coat electronics components and implants. Its thermal conductivity is $0.084 \text{ W m}^{-1} \text{ K}^{-1}$ and its emissivity is 0.8. An integrated circuit, total area 2.00 cm^2 was coated with $50 \text{ }\mu\text{m}$ of Parylene C and cooled with flowing air at $25 \text{ }^\circ\text{C}$. The convective heat transfer coefficient between the packaging and the air is $30 \text{ W m}^{-2} \text{ K}^{-1}$. The Stefan-Boltzmann constant $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. Under steady-state conditions, the surface temperature of the packaging is $70 \text{ }^\circ\text{C}$. Calculate (i) the total heat transfer to the air and (ii) the temperature of the integrated circuit where it meets the packaging material.**
55 marks
- Question total =100 marks**

- 2** **a)** What are the important physico-chemical properties of water that make it a good solvent for ionic solids?
15 marks
- b)** The solubility product, K_{sp} of silver chloride AgCl at 25 °C when the concentration units are in mol dm⁻³ is 1.8×10^{-10} .
- (i)** What is the solubility of silver chloride in water?
 (ii) What would be its solubility in 0.15 mol dm⁻³ NaCl?
35 marks
- c)** Under which circumstances does the solubility product not reliably predict the solubility of a scarcely soluble salt?
15 marks
- d)** The Henry's Law constant for hydrogen peroxide (H₂O₂) in alveolar fluid, at 37 °C is 0.700 mol dm⁻³ Pa⁻¹. During chronic obstructive pulmonary disease, the concentration of H₂O₂ in alveolar fluid has been measured at 0.60 μmol dm⁻³. What is the expected partial pressure of H₂O₂ in the breath of these patients?
20 marks
- e)** Apart from Henry's law constants, define other parameters are commonly used to quantify gas solubility in liquids? What are their limitations?
15 marks
- Question total = 100 marks**

- 3 a) The Stokes-Einstein equation is given by:

$$D = \frac{k_B T}{f}$$

Where D is the diffusion coefficient, k_B is Boltzmann's constant, T is the absolute temperature. f is the frictional coefficient which for a sphere is given by Stokes' law:

$$f = 6\pi\eta r$$

where η is the viscosity coefficient and r is the radius of the sphere.

The diffusion coefficient for immunoglobulin in buffer at 25 °C was measured as $4.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. Calculate r from the diffusion coefficient. From crystallography, its density is $1.353 \times 10^3 \text{ kg m}^{-3}$ and its molecular mass is 156,000. Use these data to calculate r and comment on the consistency the diffusion data. The viscosity of the buffer at 25 °C = $9.2 \times 10^{-4} \text{ Pa s}$. Boltzmann's constant, $k_B = 1.380658 \times 10^{-23} \text{ J K}^{-1}$. Avagadro's constant is $6.022 \times 10^{23} \text{ mol}^{-1}$.

30 marks

- b) Given the definitions of the thermodynamic variables:

$$U = H - PV$$

$$G = H - TS$$

$$A = U - TS$$

the first law of thermodynamics and the Clausius relationship:

$$dS = \frac{\delta q_{rev}}{T}$$

- (i) Derive the four fundamental property relations:

$$dU = TdS - pdV$$

$$dH = TdS + Vdp$$

$$dG = Vdp - SdT$$

$$dA = -pdV - SdT$$

Clearly state all assumptions.

25 marks

Question 3 continues overleaf

- (ii) Find an expression for $\left(\frac{\partial G}{\partial T}\right)_p$, $\left(\frac{\partial G}{\partial p}\right)_T$ and thus prove the Maxwell relation:

$$-\left(\frac{\partial S}{\partial p}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p$$

25 marks

- (iii) Find an expression for $\left(\frac{\partial S}{\partial T}\right)_V$ for an ideal gas in terms of variables that can be measured experimentally.

20 marks

Question total = 100 marks

4 a) For the first order reaction:



the instantaneous concentration of the reactant $[A]_t$ in a first order reaction where the initial concentration was $[A]_0$ is given by:

$$[A]_t = [A]_0 \exp(-kt)$$

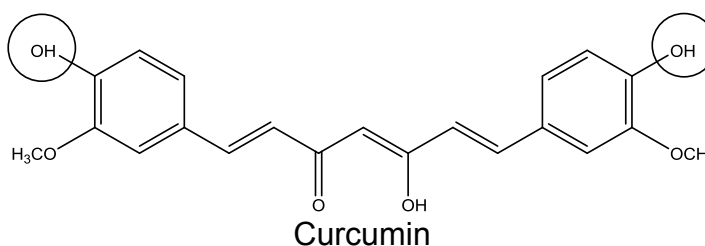
where k is the first order rate constant t is the time.

Show that the half-life $\tau_{1/2}$ is given by:

$$\tau_{1/2} = \frac{\ln 2}{k}$$

20 marks

b) The compound responsible for the yellow colour of the curry spice turmeric is curcumin:



It is widely used in traditional medicine and has been extensively investigated as a drug. One of the many problems however is its low stability in solution. Its half-lives as a function of temperature have recently been reported as 20.0 min at 25 °C and 10.0 min at 37 °C. If the decomposition is a first order reaction, calculate the rate constants at both temperatures and thus the activation energy.

40 marks

c) The concentration of curcumin can easily be determined since the intensity of its bright yellow colour scales linearly with temperature. The experimental data demonstrating the decomposition consist of measurements of the concentration of curcumin as a function of time. Sketch the expected form of these data and state how these data be tested to establish that the reaction is indeed first order?

10 marks

Question 4 continues overleaf

d) Curcumin has two ionisable phenolic groups (-OH), circled in the structure above. These can act as acids, dissociating to give protons (H⁺) and conjugate base phenolate groups (-O⁻). Their pK_a values have been reported as 8.5 and 9.5.

(i) Show how the Henderson-Hasselbalch equation:

$$pH = pK_a + \log_{10} \left(\frac{[A^-]}{[HA]} \right)$$

Can be derived from the definition of the acid dissociation constant. [HA] is the concentration of the undissociated acid, [A⁻] is the concentration of the conjugate base.

20 marks

(ii) At pH 7.5, would they be present as phenols or deprotonated as phenolates? Would you expect curcumin be more or less soluble in water at pH 7.5 than pH 10? Justify your answers.

10 marks

Question total = 100 marks

Answers

1 (a) The internal energy of an isolated system is constant: $dU = dq + dq$; any one of: when two systems are brought into contact, heat flows for the hotter to the cooler body; for any cyclic process, heat cannot be converted completely into work, though work can be completely converted to heat; for any isolated system, entropy increase for any spontaneous process; spontaneous changes are always accompanied by a conversion of energy into a more disordered form; $S = k \ln w$. 5 marks for each law. **10 marks in total.**

(b) (i) $Power = iV = 60\text{ W} = 60\text{ J s}^{-1}$. Therefore $work = 2 \times 60 \times 60 \times 60 = 4.32 \times 10^5\text{ J}$ **10 marks.**

(ii) Get the spring constant using Hooke's Law and sticking to SI units:

$$k = \frac{300}{1 \times 10^{-3}}$$

Use Hooke's law again to calculate force = 600 N.

$$work = f\Delta x = 600 \times 10^{-2} = 1.2\text{ J}$$

For 10 marks

c) Conduction: $\dot{Q} = -kA \frac{\partial T}{\partial x}$

Q heat transfer (W)

q heat flux (W/m)

k thermal conductivity (W/mK)

A area (m²)

T temperature (K)

x distance (m)

Convection: $Q = hA(T_2 - T_1)$

Q heat transfer (W)

h heat transfer coefficient (W/m².K)

T temperature (K)

Radiation:

$$Q = \sigma A(T^4)$$

Q = Heat radiated (W)

σ = Stefan-Boltzmann constant $5.67 \times 10^{-8}\text{ W/m}^2\text{K}^4$

A = Surface area of the body (m²)

T = Body temperature

5 marks per law

d) At the outside surface, the total heat transfer to the air is the sum of the convective heat, Q_{conv} and the radiative losses Q_{rad} .

$$Q_{rad} = \varepsilon \sigma A [(70 + 273.15)^4 - (25 + 273.15)^4] = 0.054 \text{ W}$$

And

$$Q_{conv} = 30 \times 2 \times 10^{-4} \times 45 = 0.27 \text{ W}$$

Total heat transfer to air = 0.324 W

For **30 marks**

The first law requires that in the steady state:

$$Q_{conv} = Q_{loss \text{ to air}}$$

Use Fourier's law and the above result and rearrange:

$$Q_{conv} = \frac{0.084 \times 2 \times 10^{-4} \Delta T}{50 \times 10^{-6}}$$

$$\therefore \Delta T = -0.964 \text{ }^{\circ}\text{C}$$

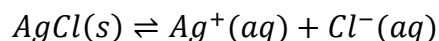
So the surface of the semiconductor is at 70.96 $^{\circ}\text{C}$ or 444.11 K.

For the remaining **25 marks**

55 marks for part (d)

2 a) High relative permittivity, high dipole moment: good solvent for ions, water molecules orientate themselves around ions to form hydrated species, large liquid range. **15 marks**

b) Write down the balanced equation for the dissolution of AgCl (s):



(i) At saturation S moles per dm^3 dissolve. Using the definition of the solubility product:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = S^2$$

Solving for S gives solubility = $1.34 \times 10^{-5} \text{ mol dm}^{-3}$

15 marks

(ii) In the presence of 0.15 mol dm^{-3} the common ion Cl^- , the equilibrium concentration of Ag^+ and Cl^- when S moles of AgCl dissolve will be S and $(S + 0.15) \text{ mol dm}^{-3}$ respectively.

$$S^2 = 0.15S - K_{sp}$$

Solving the resulting quadratic gives $S = 1.2 \times 10^{-9} \text{ mol dm}^{-3}$.

20 marks

35 marks for (b)

c) Aside from the common ion effect, the presence of complexing agents (ligands) will increase the solubility; if the anion is a conjugate ion of a weak acid, lowering the pH will also increase the solubility; if the resulting solution (or receiving solution) has a high ionic strength, solubility may differ significantly from activity. Solubility products are defined in terms of activity.

15 marks

d) From the dimensions of the Henry's law constant, it is evident that:

$$K_H = \frac{[H_2O_2]}{p_{H_2O_2}}$$

Rearrangement and solution gives $p_{H_2O_2} = 8.57 \times 10^{-7} \text{ Pa}$

20 marks

e) Other possible gas solubility parameters are Bunsen coefficient, the volume of gas dissolved in unit volume of solvent, reduced to 0 °C and 1 atm (101,300 Pa) assuming ideal gas behaviour; Ostwald coefficient: ratio of volume of gas absorbed to volume of liquid at the same temperature. The principal disadvantages are that these are both lumped parameters which include the equilibrium constant for dissolution plus any chemical reaction occurring in the solution. This prevents more serious thermodynamic analysis such as estimating temperature effects from the enthalpy and Clausius-Clapeyron equation.

10 for the parameters, 5 for the limitations, 15 marks for (e) in total.

3 (a) Use the Stokes-Einstein equation to calculate $r = 5.93 \times 10^{-9} \text{ m}$

10 marks so far

Calculate the volume of the immunoglobulin per mole from the density data, taking due account of SI units = $0.115 \text{ m}^3 \text{ mol}^{-1}$.

Divide by Avagadro's number to get the volume per particle = $1.91 \times 10^{-25} \text{ m}^3$ per molecule.

$$V = \frac{4}{3} \pi r^3$$

Solve for $r = 3.57 \times 10^{-9} \text{ m}$

The radius from the Stokes-Einstein will be the hydrodynamic radius. In this case it is substantially larger than the radius from the crystallographic data. There could be several reasons for this: in solution, there will be substantial numbers of water molecules associated with the immunoglobulin. It seems unlikely that this alone could account for such a large difference. Other possibilities are that the immunoglobulin in the crystal could have its structure affected by the preparation used; the assumption of sphericity could be wrong; all other shapes have higher viscous drag for a given volume.

30 marks in total 20 for the calculations and a further 10 for detailed discussion of the meaning of radii (r diffusion coefficients) from diffusion data and the assumptions underpinning the derivation of the Stokes-Einstein equation.

b) (i) Starting with the differential form of the first law $dU = \delta q + \delta w$ For the first of the fundamental property relationships, assume reversibility, constant p and only pV work and $w = \int p dV$, so $\delta w = -p dV$. Sub this for work into the first law, and use the Clausius expression for the heat to yield the required result $dU = T dS - p dV$. This is now generally true since it consists only of state functions.

10 marks so far

For the remaining relationships, use the definitions and the chain rule to write the differential forms:

$$dH = dU + p dV + V dp$$

Sub for dU to get:

$$dH = T dS + V dp$$

Similar approaches yield the remaining two relationships:

$$dG = V dp - S dT$$

And:

$$dA = -p dV - S dT$$

5 each for these three

Total 25 marks. Answers must include clear statements of the assumptions and maths rules employed.

(iii) $dG = V dp - S dT$ and $G(T, p)$. Write down the Euler expression for the total differential:

$$dG = \left(\frac{\partial G}{\partial p} \right)_T dp + \left(\frac{\partial G}{\partial T} \right)_p dT$$

Compare the coefficients of dp and dT :

$$\left(\frac{\partial G}{\partial p}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_p = -S$$

For state functions, the order of differentiation yields the same second order differential. Differentiate V and S with respect to p and T respectively and the resulting functions will therefore be equal:

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \text{ for } \mathbf{25 \text{ marks}}$$

(iii)

$dU = TdS - pdV$. Divide through by dT at constant volume:

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V - p\left(\frac{\partial V}{\partial T}\right)_V$$

Lose the last term, since $dV = 0$

$$dU = TdS$$

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

LHS is the definition of constant volume heat capacity, C_V :

$$=\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} C_V$$

20 marks

For an ideal monoatomic gas, $C_V = \frac{3nR}{2}$ so $\left(\frac{\partial S}{\partial T}\right)_V = \frac{3nR}{2T}$

4 a) Sub $[A]_t = [A]_0 / 2$ into the integrated rate law:

$$\frac{1}{2} = \exp(-k\tau_{1/2})$$

Take logs of both sides:

$$\begin{aligned} \ln(1/2) &= -k\tau_{1/2} \\ \therefore \ln 2 &= k\tau_{1/2} \end{aligned}$$

And $\therefore \tau_{1/2} = \frac{\ln 2}{k}$ for **20 marks**

b) Get the rate constants (in s^{-1} or min^{-1}) from the half-lives:

$$k_{T1} = 5.776 \times 10^{-4} \text{ s}^{-1} \text{ or } 0.03466 \text{ min}^{-1}$$

$$k_{T1} = 1.155 \times 10^{-3} \text{ s}^{-1} \text{ or } 0.06931 \text{ min}^{-1}$$

For 10 marks

Recalling the Arrhenius equation for the dependency of the rate constant on absolute temperature:

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

The pre-exponential A is approximately independent of temperature, as is the activation energy. This allows trivial rearrangement to give:

$$\ln\left(\frac{k_{T1}}{k_{T2}}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Enabling calculation of the activation energy $E_a = 4.44 \times 10^4 \text{ J}$

For the remaining 30 marks. 40 marks for part (a)

c) Expect an exponential relationship between concentration and time. A plot of $\ln\left(\frac{[A]_t}{[A]_0}\right)$ versus time should be linear, slope $-k$.

10 marks

d) (i) The acid dissociation constant K_a for acid HA dissociating to H^+ and A^- is defined as:

$$K_a = \frac{[H^+].[A^-]}{[HA]}$$

Recall that the p operator is $-\log_{10}$ of its argument, take p of both sides and rearrange to get the desired form of the Henderson-Hasselbalch equation.

20 marks

(ii) When the $pH = pK_a$ the phenol and phenolate species will be present at equal concentrations. $pH 7.4$ is some way below both of the quoted pK_a values so both moieties will be protonated. Whilst these will still be capable of hydrogen bonding, it is expected that this is more likely to cause aggregation and in any case will show lower solubility than the deprotonated form dominating at $pH 11$. Since $pH 7.4$ is close to the expected pH of typical sites of action of any drug and high pH administration is out of the question, low solubility and possibly drug aggregation would be expected at physiological pH . Another reason, aside from the instability, why curcumin is not really a drug candidate.

The answer must include: the effects of ionisation on solubility, interpreting the pK_a and its use in predicting ionisation state, likely aggregation and thus unsuitability as a drug

10 marks