IMPERIAL COLLEGE LONDON

B.Eng., M.Eng and ACGI Examinations 2016
Part 1

Biomedical Engineering
BE1-HHMT1 Heat & Mass Transport 1

Tuesday, 00 Month 2016   00.00 -14.30pm

Duration: 1.5 hour

The paper has FOUR questions.

Answer <u>ALL FOUR</u> 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 $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

Gas constant, R = 8.314 J K mol^{-1}
0 °C = 273.15 K
Boltzmann's constant k_B= 1.380658 × 10^{-23} J K^{-1}
Avagadro's number, N_A = 6.022 × 10^{23} mol^{-1}
The permittivity of free space is 8.85 × 10^{-12} F m^{-1}
The Stefan-Boltzmann constant 5.67x10^{-8} W/m^{2}K^4
The charge on an electron is 1.60 × 10^{-19} C or 9.647 × 10^4 C mol^{-1}.

1   **a)** State the first two laws of thermodynamics.

10 marks

b) For a perfect gas, show that the entropy change when it is compressed from p_A to p_A is given by:

$$\Delta S = -nRln\frac{p_B}{p_A}$$

Calculate the entropy change when 1 dm³ of helium at one atm is compressed from 1 atm to 5 atm at a constant temperature of 298 K. [1 atm. = 101,300 Pa]. Clearly state all assumptions. Comment on the result.

20 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) Human skin can be considered as three layers from the inside outward consisting of fat, dermis and epidermis. The properties of a typical piece of human skin are tabulated below:

Tissue	Thickness/ mm	Thermal conductivity/ W m^{-1} K^{-1}
Fat	10	0.22
Dermis	2.0	0.20
Epidermis	1.0	0.31

If the innermost surface of the fat is at 35 °C and the outermost layer of the epidermis is at 10 °C, calculate (i) the steady state heat flux across 1 cm² of skin (ii) the temperature at the fat: dermis boundary.

55 marks

2   **a)** Iron (II) hydroxide dissolves in water as:

$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$$
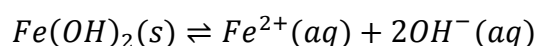
The ionic solubility product, K_{sp} for iron (II) hydroxide in water at 25 °C is 7.0×10^{-16}. What is its solubility? What would the pH be of a saturated solution? The autoionisation constant of water, $K_W = 1.00 \times 10^{-14}$.

30 marks

b) The pK_a of the amino acid glycine is 2.351. What would the pH of a 5 mmol dm^{-3} solution of glycine in water be?

30 marks

c) The carbon dioxide concentration of dry air of my lab was measured as a slightly alarming 610 ppm. The total air pressure was measured as 101,300 Pa and the temperature was 298 K.

   (i)   What would be the concentration of dissolved carbon dioxide in the de-ionised water be?
   (ii)   What would its pH be?

DATA The Henry's Law constant of CO_2 at 25 °C is $K_H = 3.3 \times 10^{-7}$ mol dm^{-3} Pa^{-1}. The first acid dissociation constant for CO_2 (aq), $K_a = 4.2 \times 10^{-7}$ mol dm^{-3}. The vapour pressure of water at 25 °C is 3167 Pa.

40 marks

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

$$D = \frac{kT}{f}$$

Where D is the diffusion coefficient, k is Boltzmann's constant, T is the absolute temperature and f is the frictional coefficient. By considering the free energy differences arising from a concentration gradient, given that the viscous drag force, F for a body moving at velocity v is $F = fv$, show how this equation can be derived.

40 marks

b) What are the key physical and mathematical properties of a state function?

20 marks

c) For a system that only does pV work, the differential form of the first law of thermodynamics can be written as:

$$dU = TdS - pdV$$

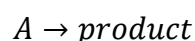From the definition of enthalpy, H:

$$H = U + pV$$

derive the Maxwell Relationship:

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

40 marks

4 **a)** For the first order reaction:

$$A \rightarrow product$$

Show that the instantaneous concentration of the reactant $[A]_t$ in a first order reaction where the initial concentration was $[A]_0$ is given by:
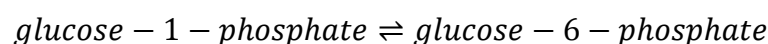
$$[A]_t = [A]_0 exp(-kt)$$

20 marks

b) Explain how the Ostwald isolation method and the method of initial rates are used to deduce the experimental rate law.

20 marks

c) The following reaction is catalysed by the enzyme phosphoglucomutase:

$$glucose - 1 - phosphate \rightleftharpoons glucose - 6 - phosphate$$

The equilibrium constant is 19.0.

(i)   What is the value of the standard free energy, ΔG^o when the temperature is 298 K?

15 marks

(ii)   What is the value of ΔG if the glucose-1-phosphate is maintained at 10 mM and the glucose-6-phosphate is kept at 1 mM?

10 marks

(iii)   How is the equilibrium constant related to the rate constants for the forward and backward reactions.

15 marks

(iv)   Sketch the free energy-reaction coordinate curve for the enzyme-catalysed reaction.

20 marks

1 a) 1) The energy of an isolated system is constant.
2) When two systems are brought into thermal contact, heat flows spontaneously from the one at the higher temperature to the one at the lower temperature.
OR
2) Heat cannot be completely converted into work for any cyclic process, but work can be completely converted into heat.
OR
2) Spontaneous changes are always accompanied by a conversion of energy into a more disordered form.
OR
The entropy, S, of an isolated system increases during any spontaneous change or process.
For 10 marks

b) From the First Law, $dU = dq_{rev} - pdV$ is the system only does pV work. For one mole of a perfect gas, $dU = C_V dT$ and $pV = RT$.

$$dS = \frac{dq_{rev}}{T} = C_V \frac{dT}{T} + R \frac{dV}{V}$$

$$\Delta S = S_B - S_A = C_V \ln\frac{T_B}{T_A} + R \ln\frac{V_B}{V_A}$$

At constant temperature, dT is zero so we lose the first term. Substituting for volume from the ideal gas equation gives the desired result. Use the ideal gas equation, the initial volume (in m^3) to deduce that there are 0.0408 mol of gas. Sub these values into the equation:

$$\Delta S = -nR\ln\frac{p_B}{p_A} = -0.0408 \times 8.314 \times \ln5 = -0.546 \, JK^{-1}$$

The result is negative as expected. Ideal gas behaviour has been assumed throughout. Whilst reversibility was required for the initial formulation, all the final variables are stagte functions, so this will be generally true. **20 marks**

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

Q heat transfer (W)
        q heat flux (W/m)
k thermal conductivity (W/mK)
A area (m^2)
T temperature (K)
x distance (m)

Convection, Newton: $Q = hA(T_2 - T_1)$
Q heat transfer (W)
h heat transfer coefficient (W/m^2.K)
T temperature (K)

Radiation, Stefan-Boltzmann:

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

Q = Heat radiated (W)
σ = Stefan-Boltzmann constant 5.67×10^{-8} W/m²K⁴
A = Surface area of the body (m²)
T = Body temperature **5 marks per law**

c)

1 d) Model the heat flux as occurring through two resistances in series, the conductive resistance given by $\Delta x/kA$. Convert the dimensions into SI units: 1 mm = 10^{-3} m² and 1 cm² = 10^{-4} m². Calculate the resistance of each layer:

$$R_{fat} = \frac{10 \times 10^{-3}}{0.22 \times 10^{-4}} = 454.5$$

$$R_{dermis} = \frac{2 \times 10^{-3}}{0.20 \times 10^{-4}} = 100$$

$$R_{epi} = \frac{1.0 \times 10^{-3}}{0.31 \times 10^{-4}} = 32.26$$

The total resistance is 586.76. The temperature drop across the composite is 25 K. Calculate the total conductive heat flux from:

$$Q = \frac{\Delta T}{\Sigma R}$$

= 0.043 W cm⁻².

20 marks for formulating the problem correctly as two series resistances to heat flow. A further 20 marks for correctly executing the arithmetic, including units and significant figures.

Q will be, from energy conservation, the same through all three layers. The temperature drop through the fat can therefore be calculated from:

$$\Delta T = QR_{fat} = 19.3\,K$$

Since the inside temperature is 35 ºC, the temperature of the fat: dermis boundary is 15.6 ºC. For a further 15 marks

55 marks for part (d) in total

2 a) S moles of $Fe(OH)_2$ dissolve to form S moles of Fe^{2+} and $2S$ moles of OH^-. By definition:

$$K_{sp} = [Fe^{2+}].\,[OH^-]^2$$
$$= 4S^3$$
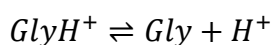$$\therefore S = \sqrt[3]{\frac{K_{sp}}{4}} = 5.6 \times 10^{-6} mol\,dm^{-3}$$

For 15 marks

$[OH^-]$ = 1.11 × 10^{-5} mol dm^{-3}. So pOH = 4.95, so pH = 9.05

For the remaining 15 marks.

b) Write down the reaction for the dissociation:

$$GlyH^+ \rightleftharpoons Gly + H^+$$

By definition:

$$K_a = \frac{[Gly][H^+]}{[GlyH^+]}$$

If x mol dm^{-3} of the protonated glycine are dissociated at equilibrium, then the concentrations of the three species are (5 × 10^{-3}), x and x respectively. Substitute into the equation for the dissociation constant and solve the resulting quadratic (taking the positive root) to get x = 2.99 × 10^{-3} mol dm^{-3}. The pH is therefore 2.52. For 30 marks.

c) $p(total)$ = 101,300 Pa. p (CO$_2$) = 600 × 10^{-6} (101,300 − 3167)

From the dimensions of the unit, the concentration of CO_2 is given by:

$$K_H = \frac{[CO_2(aq)]}{pCO_2} = 1.94 \times 10^{-5} mol\,dm^{-3}$$

For 20 marks

The pCO$_2$ is fixed due to the essentially limitless supply from the large atmosphere. The acid dissociation constant is given by:

$$K_a = \frac{[H^+][HCO_3^-]}{[CO_2]}$$

Use the carbon dioxide concentration from (i) and note that the bicarbonate concentration and proton concentration are the same, x.

$$K_a = \frac{x^2}{1.94 \times 10^{-5}}$$

x = 2.85 × 10^{-6} mol dm^{-3}. So the pH = 5.54
For 20 marks.

3 a) Consider the difference in free energy over distance dx where the concentration changes from c to $(c + dc)$. Calculate the difference between molar Gibbs energy at c and that at $(c + dc)$:

$$dG = G_{c+dc} - G_c = RT \ln\left(\frac{c+dc}{c}\right) = RT \ln\left(1 + \frac{dc}{c}\right)$$

Since dc is small:

$$\ln\left(1 + \frac{dc}{c}\right) \approx \frac{dc}{c}$$

$$\therefore dG = \frac{RTdc}{c}$$

Therefore the work done **by** the system, -w to move one molecule from $c + dc$ to c is:

$$-w = \frac{-k_B T dc}{c}$$

Work, -w, is done over distance dx, if F is the driving force, $-w = Fdx$. The driving force is thus given by:

$$F = -\frac{k_B T}{c}\frac{dc}{dx}$$

At constant velocity, $F = fv$, where f is the <u>frictional coefficient</u>. The limiting velocity is obtained when the frictional force is equal to the driving force:

$$fv = -\frac{k_B T}{c}\frac{dc}{dx}$$

$$cv = -\frac{k_B T}{f}\frac{dc}{dx}$$

But cv = flux.

$$J = \frac{-k_B T}{f}\frac{dc}{dx}$$

Comparison with Fick's Law reveals:

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

For **50 marks**

3 b) Physically the value of a state function is independent of the path taken. Examples include pressure, volume, temperature which for a fixed amount of material define the physical state of an ideal gas. Three important mathematical properties are: (i) For any state function *X*, *dX* is an exact differential and therefore the integral:

$\Delta X = \int_A^B dX$ has a definite value independent of the path taken from A to B.

(ii) We can write the total differential of the function $U(X,Y)$ as:

$$dU = \left(\frac{\partial U}{\partial X}\right)_Y dX + \left(\frac{\partial U}{\partial Y}\right)_X dY$$

(iii) The order of differentiation does not matter, so:

$$\frac{\partial^2 U}{\partial X \partial Y} = \frac{\partial^2 U}{\partial Y \partial X}$$

20 marks

Write down the differential form of the definition of enthalpy:
$dH = dU + pdV + Vdp$ (1)
From the fundamental property relationship:
$dU = TdS - Vdp$ (2)
Substitution from this into (1) gives:
$dH = TdS + Vdp$ (3)
.
Next, write down the Euler expression for $H(S, p)$ since these are our target variables:
$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$ (4)
Comparison of the coefficients of (4) with (3) above shows:

$$\left(\frac{\partial H}{\partial S}\right)_p = T \text{ and } \left(\frac{\partial H}{\partial p}\right)_S = V$$

Since these are all state functions and therefore the second derivatives will be identical regardless of order of differentiation, differentiate T w.r.t. *p* and *V* w.r.t. *S* to yield the required Maxwell relation. **40 marks**.

4 a) The reaction is given by: $A \rightarrow Products$ and the rate law, using the principle of mass action can be written by inspection:

$$v = -\frac{dA}{dt} = k[A]$$

Separation of the variables enables integration:

$$\int_{A_0}^{A} \frac{d[A]}{[A]} = -kt$$

$$-kt = ln\left(\frac{[A]_t}{[A]_0}\right)$$

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

For 20 marks.

4 b) Make all bar one reactant species present to large excess so that their concentrations will not change during the course of the reaction. The reaction will then be pseudo-first order. This can then be repeated to limit each reactant in turn. For the method of initial rates, take the initial rate v_0 at $t = 0$. If the initial rate is given by:

$$v_0 = k[A]_0^a$$

Plotting the log of the initial rate against the log of the initial concentration for a range of concentrations allows calculation of the exponent, the order with respect to [A].

20 marks

4 c) $$\Delta G = \Delta G° + RT lnK$$

At equilibrium, $\Delta G = 0$.

$$\therefore \Delta G° = -RT lnK = -7205 \, J \, mol^{-1}$$

For 15 marks.

(ii)   Use the result from (i) and the original equation:

$$\Delta G = -7295 + 8.314.298.\ln(0.1) = -13 \, kJ \, mol^{-1}$$

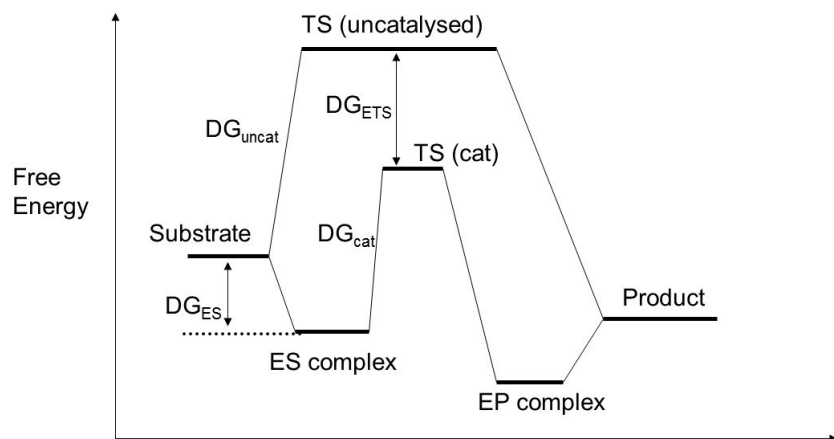For 10 marks

(iii) $$v(forward) = -k[reactant]$$
$$v(backward) = -k[product]$$

At equilibrium,

$$-k_1[reactant] = -k_{-1}[product]$$
$$\frac{k_1}{k_{-1}} = \frac{[reactant]}{[products]} = K$$

For 15 marks

For 20 marks. Key ideas are: the transition state energy is lowered by the formation of a TS-enzyme complex. The substrate-enzyme complex must also be lower in free energy to enable spontaneous formation. The lowering of the TS energy must be larger than the lowering due to substrate binding.
For 20 marks