3.4 Using the simplified formula $R_t = (RT/F)/(j_e zA)$ gives $0.025/(0.8 \times 10^{-2} \times 2 \times 10^{-4}) = 15.6$ kΩ. (N.B. 0.8×10^{-3} mA/cm^2 = 0.8×10^{-2} A/m^2; 2 cm^2 = 2×10^{-4} m^2). Note that in this case $J/2j_e = 1/1.6$, so $\sinh^{-1}(1/1.6)/(1/1.6) = 0.94$, so $R_t = 2(RT/F) \times .94/(z \times J \times A) = 2 \times 0.025 \times .94/2 \times 10^{-6}$, since J.A is the actual current drawn. This gives 23 kΩ.

3.5 Use a plotting program to plot $\ln(J)$ on the y-axis and η on the x axis. The limiting slope is equal to $zF\alpha/RT$, or $2\alpha/25$, since the ordinate is in mV. In this case the slope is .04, so the value for α is 0.5, approximately. The value of j_e is given by the intercept, or $\ln^{-1}(-.25) = 0.78$. This is to be interpreted as μA/cm^2. Since the limiting current density is approximately 30 times the maximum current density drawn in this experiment, it is unlikely that the concentration overpotential will influence the analysis significantly.

3.6 i) when both electrodes have the same impedance, the output voltage v_o due to the 10 V interference will be $10^3 \times 10/10^5 = 0.1$V
ii) using the equation in the text we get:
$v_o = 10^3 \times 10[(1.1 - 1.0)\times 10^4/10^7 + 1/10^5] = 10^4[10^{-4} + 10^{-5}]$ or 1.1 V pp approximately.

3.7 a)The current density is $200/(2 \times 2) = 50$ mA/cm^2. Using the approximate formula $J = j_e(zF\eta/RT)$ gives $j_e = 50 \times 25/200 = 6.25$ mA/cm^2. Using the more complicated equation (with the sinh term) gives 3.64 mA/cm^2. In this case the simple equation should not be used.
b) Using the approximate formula $R_c = [RT/(zFA)]/(J_L - J)$ gives $[.025/4 \times 10^{-4}/[(80 - 200/4) \times 10^{-3} \times 10^4] = 21$ Ω (note that the amounts need to be changed to V and A/m^2). If the concentration were to rise 10-fold, then J_L would do the same and the resistance would drop to around 0.8Ω.

Chapter 5

5.1 a) 1.6×10^{-10}
c) 5.2×10^{-8}; 8.0×10^{-8} m^2/s/V
d) 10^{-8} m

5.2 Concentration gradient is dc/dx
i) $dc/dx = 3 \times 0.05 x^2 = 0.15$ mol.m^4 at $x = 1$
ii) $J = 1.5 \times 10^{-4}$ mol/m^2/s
$\quad J = -D\, dc/dx$, so $D = |J|/(dc/dx)$
$\qquad = 1.5 \times 10^{-4}/0.15$ (mol/m^2/s/(mol/m^4)) $= 10^{-3}$ m^2/s

5.3 Using the relationship $D = uRT/(|z|F)$ and remembering that RT/F = 0.025 V (25 mV) we easily show that $7.91 \times 10^{-4} \times .025 = 2 \times 10^{-5}$ cm^2/s or 2×10^{-9} m^2/s. If we now use the Einstein-Sutherland relationship $D = RT/(6\pi\eta aN)$, then using the values given at the start of this manual (and assuming t = 300K) we get $a = RT/(D6\pi\eta N) = 8.31 \times 300/(2 \times 10^{-9} \times 6\pi \times 10^{-3} \times 6 \times 10^{23}) = 1.1$ pm

5.4 i) If the membrane is non-selective and the two solutions have the same concentration, then pd = 0
ii) The pd will be given by the expression for diffusion potential:
$\qquad V_{12} = (RT/F).[(u^- - u^+)/(u^- + u^+)].\ln (c_2/c_1)$
$\qquad = 25.[(7.91 - 4.01)/(7.91 + 4.01)]. \ln (0.02/0.1)$
$\qquad = 25[3.91/11.92].(-1.61) = -13.1$ mV (i.e. side 2 is -ve)
iii) If only Li$^+$ is permeating the membrane, then u$^-$ = 0 and

V_{21} = (RT/F).(-1).ln (0.02/0.1) = 25.(-1).(-1.61) = +40 mV (side 2 now +ve)

iv) If only H_2O permeates, then Li^+ and Cl^- are acting as osmotic particles
Osmotic pressure (OP) of side 1 = RT(0.1 + 0.1) x 10^3

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad Li^+\uparrow\quad Cl^-\uparrow\quad \uparrow$converts to mol/m³

OP of side 2 = RT(0.02 + 0.02) x 10^3
Difference (which equals the amount of pressure to be applied to prevent movement)
ΔOP = RT(0.2 - 0.04) x 10^3
= 8.31 x 298 x 160 = 0.396 MPa (3.8 Atm)

5.5   We have to assume that Br^- exchanges with Cl^-, so that the Ag/AgCl electrode effectively measures $[Br^-]$. The difference between the two half-cell potentials is thus -58 log (.5/.005) = 116 mV. However, there is also a liquid junction potential associated with the 3M NaBr/Agar bridge. In fact there is a liquid junction potential at either end of the bridge, but the net effect is a liquid junction between two solutions, 0.5 and 0.005 M. Using the liquid junction formula V_{21} = $[(u^- - u^+)/(u^- + u^+)].(RT/F).ln (c_2/c_1)$ gives [(8.13 − 5.19)/(8.13 + 5.19)] x 116 = +26 mV. Adding these together gives - 90 mV.
Since NaBr completely dissociates, the osmotic pressure is given by the sum of the two ion concentrations times RT. The difference between the two sides is thus 8.31 x 300 x 2 x (.5 - .005) x 10^3 = 2.47 MPa. This pressure should be added to the more concentrated side.

5.6   a) i) This system is in steady state (because the compartments 1 & 2 are so large that the concentrations don't change) but since Na^+ and Cl^- are continuously diffusing across the membrane an equilibrium is never reached.
ii) If u_{Na} = 0 the Cl^- ceases to diffuse because of the necessity to preserve neutrality, but a Nernst potential develops preventing diffusion of Cl^-. This is an <u>equilibrium</u> state (the energy of the Cl^- solution, or electrochemical potential, is the same both sides of the membrane.

b) i)   The mathematical expression for u_{Cl} > 0 and u_{Na} > 0 is:
$\qquad J_{Cl} = - u_{Cl} (RT/F)(dc_{Cl}/dx) + u_{Cl}c_{Cl}dV/dx$

ii)   Derivation of the liquid junction equation is given in section 3.2: assumes
$\qquad\qquad J_{Cl} = J_{Na}$ and $c_{Cl} = c_{Na}$

5.7   a) See text
b)The hydrated ion radii can be used to estimate mobility from the Stokes-Einstein eqn.   D = (uRT)/(|z| F) = RT/(6$\pi\eta$aN);   i.e. u = |z| F/(6$\pi\eta$aN) = |z| e/ (6$\pi\eta$a)
where e is electronic charge. Assume viscosity (although in this case it is not needed) to be that for pure water (10^{-3} Pa.s)

Diffusion potential = (RT/F)[$u^- - u^+$)/($u^- + u^+$)]ln(c/c′)

= (RT/F). <u>$[ze/(6\pi\eta)\{1/a^- - 1/a^+\}]$</u>. ln (100/10)
$\qquad\qquad [ze/(6\pi\eta)\{1/a^- + 1/a^+\}]$

= 25.   <u>$\{1/110 - 1/164\}$ x 10^{+12}</u> . x 2.303 (mV) = 58 x 0.197
$\qquad\quad \{1/110 + 1/164\}$ x 10^{+12}

= 11.44 mV (side 2 +ve)

5

The Ag/AgCl electrodes are sensitive to Cl^- ions. In the absence of a diffusion or liquid junction potential, of $-25 \ln (100/10)$ or $-58 \log (100/10) = -58$ mV (side 2 -ve) would be measured. Total pd is thus $-58 + 11.44 = -46.6$ mV

5.8   Since the ions dissociate, the number of mOsm/l is the sum of the cations $(120 + 2 + 1 + 1)$ and the anions $(120 + 2 + 2 + 1)$ (note that when $CaCl_2$ dissociates, it yields 2 Cl^- ions for 1 Ca^+ ion. The total is thus 249 mOsm/l, with 124.5 mOsm/l on the other side (difference being 124.5 mOsm/l or 124.5 Osm/m^3, which can be converted to 0.31 MPa by multiplying by RT (8.31 x 300): to the more concentrated side

5.9   a) Because passage through the membrane is related to the ease with which substances dissolve in the phopholipid bilayer. Small ion and water permeate much faster than expected, because they diffuse through water-filled channels or pores through the bilayer.

$K^+ = ?$ $Cl^- = ?$ $R^{4-} = 10$ Side 1	$K^+ = 100$ $Cl^- = 100$ Side 2

b) There are two conditions which have to be satisfied:
i) Donnan: $K_1/100 = 100/Cl_1$
ii) electroneutrality: $K_1 = Cl_1 + 4 \times 10$ (in mM)
$\qquad$ i.e. $K_1 = (100)^2/K_1 + 40$
$\qquad K_1^2 - 40 K_1 - 10^4 = 0$

$$K_1 = \frac{40 \pm \sqrt{\{(40)^2 - 4.(-10^4)\}}}{2}$$
$\qquad K_1 = (40 + 204)/2 = 122$ mM (since -ve nos. can be ignored)
$\qquad$ thus $Cl_1 = 122 - 40 = 82$ mM
(Check: $122/100 = 100/82$)
PD is given by: $(RT/F).\ln (K_1/K_2) = -(RT/F).\ln (Cl_1/Cl_2) = 58 \log(122/100) = 5$mV

c) Osmotic pressure $= 7.479 \times 10^5$ Pa $= RT(c_{Na} + c_{Cl})$

$\qquad c_{Na} + c_{Cl} = 7.479 \times 10^5/(8.31 \times 300) = 300$

$\qquad$ Conc of NaCl $= 300/2 = 150$ mol/m^3
$\qquad$ 1 mole weighs 58.5g, so we need $150 \times 58.5 = 8.775$ kg/m^3 or 8.775 g/l

5.10   The difference of electrochemical potentials between the two sides represents the amount of work that is required to transport 1 mole against an electrochemical gradient.
$\mu_1 = \mu^* + RT.\ln(10^{-3}) + 2 \times F \times 0$
$\mu_2 = \mu^* + RT.\ln(20.086 \times 10^{-3}) + 2 \times F \times 0.1$
Thus $\mu_2 - \mu_1 = RT.\ln(20.086) + F \times .2 = 26.8$ kJ (assuming $T = 27^0C$).

5.11   i) $K_{in}/K_{out} = 1.138$, so $K_{in} = 341.4$ mM
ii) The inverse ratio hold for Cl^-, so Cl_{out}/Cl_{in} thus Cl^- is 263.6 mM. There is also 10 mM protein making 615 mOsm/l in toto.
iii) This is given by the Nernst equation $V_{out} - V_{in} = 25.\ln(1.138) = 3.2$ mV

iv) The difference in cation and anion concentration inside the bag is 341.4 – 263.6 = 77.8 mM or 80 mM approximately. Since the protein concentration is 10 mM, it must have a positive valence of 8 to maintain neutrality.

5.12   **a) The Hodgkin-Katz equation is a simplified version of the Goldman equation**

$V_{oi} = (RT/F).\ln\{[K_{in}] + \alpha[Na_{in}]\}/\{[K_{out}] + \alpha[Na_{out}]\}$

or $\exp(V_{oi}F/(RT)) = \{[K_{in}] + \alpha[Na_{in}]\}/\{[K_{out}] + \alpha[Na_{out}]\} = \exp(90/25) = 36.6$

so, $124 + \alpha \times 10.4 = 36.6 \times 2.3 + \alpha \times 36.6 \times 110$

thus $(4026 - 10)\alpha = 124 - 84$; hence $\alpha = \mathbf{0.01}$

b) The formula $P = j_{in}(1 - e^{-\Psi})/(c_{out}\Psi)$ **where** $\Psi = zFV/(RT)$ **is used, taking** Ψ **as positive if the movement of** K^+ **is aided. In this case influx is aided (inside negative) so** $P = 55 \times 10^{-9} \times (1 - e^{(-90/25)})/(2.3 \times (90/25)) = \mathbf{6.5 \times 10^{-9}}$ **m/s; this is then multiplied by 0.01 (6.5 x 10^{-11} m/s) to get** P_{Na}**. Remember to convert concentrations to mol/m³.**

5.13

Side 2   2 mmol/l

Side 1   130 mmol/l

-

+ 90 mV

$j_{2\to1} = 9 \times 10^{-12}$ mol/cm²/sec $= 9 \times 10^{-8}$ mol/m²/s.

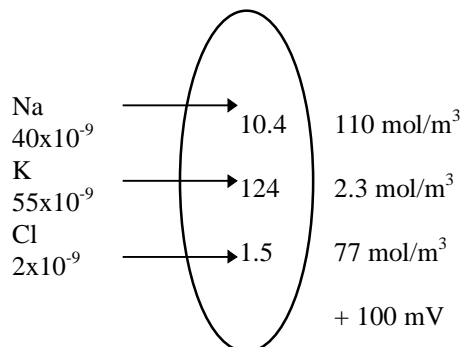Using the 'rule of thumb' we make E (or V) +ve since flow <u>in</u> is assisted by the -ve potential inside.

$f' = [FE/RT]/[1 - e^{-(FE/RT)}] = [+90/25]/[1 - e^{\{-90/25\}}] = 3.6/[1 - .027] = 3.7$

$P = j_{1\to2}/[c_2 f'] = 9 \times 10^{-8}/[2 \times 3.7] = 1.2 \times 10^{-8}$ m/s. (Don't forget: c in mol/m³).

Nernst potential for K^+: $E_K = [RT/F]\ln(130/2) = 25\ln(65) = 105$ mV, outside +ve.

5.14

Na
40×10^{-9}

K
55×10^{-9}

Cl
2×10^{-9}

10.4   110 mol/m³

124   2.3 mol/m³

1.5   77 mol/m³

+ 100 mV

Goldman factors in this case have positive pd for cations (movement assisted) and -ve pd for Chloride, which is <u>retarded</u> by negative charge inside cell.

$f_{Na} = f_K = (100/25)/[1 - e^{-(100/25)}] = 4.07$:

$f_{Cl} = (-100/25)/[1 - e^{(+100/25)}] = (-4)/(-53.6) = .075$

$P_{Na} = 40 \times 10^{-9}/(110 \times 4.07) = 8.9 \times 10^{-11}$ m/s

$P_K = 55 \times 10^{-9}/(2.3 \times 4.07) = 5.88 \times 10^{-9}$ m/s

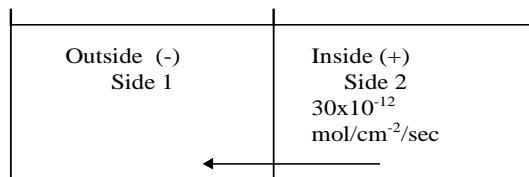$P_{Cl} = 2 \times 10^{-9}/(77 \times 0.075) = 3.46 \times 10^{-10}$ m/s

$P_{Na}/P_K = 0.015$: $P_{Cl}/P_K = 0.059$

7

E = 25. ln {[2.3 + .015x110 + .059x1.5]/ [124 + .015x10.4 + .059x77]} = 87 mV

5.15 For the three ions we use the formula $P = j_{in}(1 - e^{-\Psi})/(c_{out}\Psi)$ where $\Psi = zFV/(RT)$, taking Ψ as positive if the movement of the ion is aided (which it is for Na^+ and K^+). Thus $P_{Na} = 40$ x 10^{-9} x $(1 - e^{-4})/(110$ x $4) = 8.9$ x 10^{-11} m/s; $P_K = 55$ x 10^{-9} x $(1 - e^{-4})/(2.3$ x $4) = 5.6$ x 10^{-9} m/s; $P_{Cl} = 2$ x $10^{-9}(1 - e^{+4})/(-77$ x $4) = 3.5$ x 10^{-10}m/s. Substituting these values into the Goldman equation gives:
$V_{oi} = 25.\ln[\{8.9$ x 10^{-11} x $10.4 + 5.6$ x 10^{-9} x $124 + 3.5$ x 10^{-10} x $77\}/\{8.9$ x 10^{-11} x $110 + 5.6$ x 10^{-9} x $2.3 + 3.5$ x 10^{-10} x $1.5\}] = 86$ mV
The Nernst (or equilibrium potentials for Na, K and Cl are -59, +100 and + 98 mV respectively, so the second two will be in Donnan equilibrium ($124/2.3 = 77/1.5$, remembering to invert the anion ratio).

5.16 a) i) Following the methodology of the previous problem, $P_{Na} = 0.008$ x $(1 - e^{-1})/(150$ x $1) = 3.4$ x 10^{-11} m/s and similarly for the other 2 (sign change for Cl^-)
ii) as previous, $V_{oi} = 25.\ln[\{3.4$ x 10^{-11} x $15 + 3.8$ x 10^{-9} x $30 + 3.2$ x 10^{-9} x $160\}/\{3.4$ x 10^{-11} x $150 + 3.8$ x 10^{-9} x $10 + 3.2$ x 10^{-10} x $60\}] = -24.4$ mV
iii) As previously, using the Nernst formula gives 58; -27.7; -24.7 mV respectively
v) Na^+ is the anomaly, thus is actively transported
b) See text.

5.17

$E_{21} = E_2 - E_1 = +50 - 0 = +50$ mV
Nernst potl. $E_N = (RT/zF) \ln(c_1/c_2) = 0$, since $c_1 = c_2$

$j_{21} = 30$ x 10^{-12} mol/cm²/s = 30 x 10^{-8} mol/m²/s
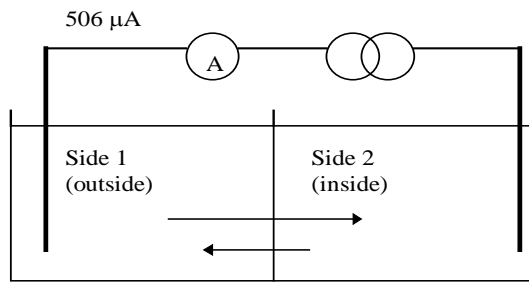$(RT/zF) = -25$ mV, since z for Cl^- is -1, so:

$\ln(j_{12}/30$ x $10^{-8}) = (0 - (+50))/(-25) = +2$

$(j_{12}/30$ x $10^{-8}) = e^{+2} = 7.39$
so influx $(j_{12}) = 2.22$ x 10^{-6} mol/m²/s. Actual value might differ from this if the movement is not passive or independent (for example, if facilitated or exchange diffusion is taking place).

5.18 a)
b) Using the formula $G_i = z^2F^2(j_{out} - j_{in})/\{RT.\ln(j_{out}/j_{in})\}$ gives $G_i = (-1)^2$ $(96,500)^2$ x $(29 - 6.1)$ x $10^{-9}/(8.31$ x $300 \ln(29/6.1)) = 0.055$ S/m²

5.19

506 µA

Side 1
(outside)

Side 2
(inside)

a) $j_{Na(12)} = 822 \times 10^{-12}$ mol/cm²/s $= 822 \times 10^{-8}$ mol/m²/s

$j_{Na(21)} = 83 \times 10^{-8}$ mol/m²/s

The difference in Na fluxes can be expressed in electrical units as:

$I'_{Na} = zFJ = zF(j_{21} - j_{12}) = 1 \times 96500 \times (822 - 83) \times 10^{-8} = 0.713$ A/m²

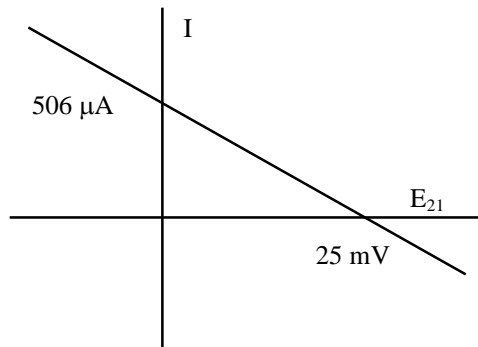$I_{Na} = I'_{Na}. A = 0.713 \times 7 \times 10^{-4} = 499$µA. Since short-circuit current = 506 µA, the net Na⁺ flux accounts for 499/506 = 98.6% of the scc.

b) As in previous example, $E_N = 0$, since concentrations are the same both sides; $E_{21} = + 25$ mV; $(RT/zF) = - 25$.

$(j_{12}/j_{21}) = \exp((0 - 25)/(-25)) = \exp(+1) = 2.718$
$j_{12} = 2.718 \times j_{21} = 2.718 \times 92 \times 10^{-8} = 250 \times 10^{-8}$ mol/m²/s

c)   We can assume that the net current through the skin varies linearly with voltage as shown:

$G = I'/E_{21} = (I/A)/E_{21} = (506 \times 10^{-6}/7 \times 10^{-4})/25 \times 10^{-3} = 28.9$ S/m²

Chloride conductance $= [z^2F^2/ (RT)].(j_{12} - j_{21})/ \{\ln(j_{21}/j_{12})\}$
$= [96500/.025].(250 - 92) \times 10^{-8} / \{\ln(250/92)\} = 6.1$ S/m², i.e. 21% of total conductance.
(N.B. the factor RT/F has to be in volts for the dimensions to be correct).

5.20   a) i) Cl efflux will be the same as influx under short circuit conditions, hence 0.28 µmol/m²/s; ii) The difference between Na⁺ influx and efflux equals the short circuit current converted to the same units. Thus 253 µA converts $(J = I/(F.A)$to $253 \times 10^{-6}/(96500 \times 6.7 \times 10^{-4}) = 3.9$ µmol/m²/s. Subtracting this from the j^{NA}_{in} given yields 0.30 µmol/m²/s; iii) Since $j^{Cl}_{in} = j^{Cl}_{out}$ we can use the simplified equation $G_i = F^2j_{Cl}/(RT) = (96500)^2 \times 0.28 \times 10^{-6}/(8.31 \times 300) = 1.05$ S/m²; iv) Skin conductance is given by $I/(A.V) = 253 \times 10^{-6}/(6.7 \times 10^{-4} \times .058) = 6.51$ S/m²

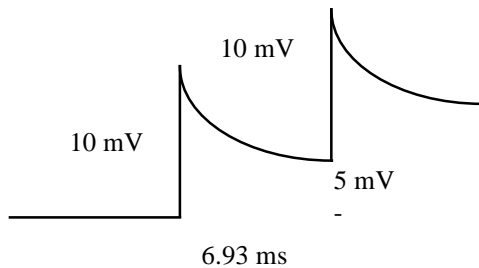b) i) From the flux ratio equation, $(j_{out}/j_{in}) = (c_{in}/c_{out}).\exp(- zFV_{oi}/(RT))$ and remembering that $c_{in} = c_{out}$, the flux ratio is $\exp(-(-1) \times (-58)/25) = 0.1$. Since $j^{Cl}_{in} = 1$ µmol/m²/s, j^{Cl}_{out} must be 0.1 µmol/m²/s ; ii) Chloride conductance =

$[z^2F^2/(RT)].(j_{12} - j_{21})/ \{\ln(j_{21}/j_{12})\}$
$= [96500/.025] \times (1 - 0.1) \times 10^{-6} / \{\ln(1/0.1)\} = 1.5 \text{ S/m}^2$

5.21 a) i) As above, the scc is first converted to flux units (J = 220 x 10^{-6}/(7 x 10^{-4} x 96500) = 3.26 μmol/m^2/s. To get j^{Na}_{in} we add on the given value of j^{Na}_{out} giving 3.63 μmol/m^2/s; ii) As before, $j^{Cl}_{in} = j^{Cl}_{out}$ = 0.52 μmol/m^2/s; iii) Using G_i = $F^2 j_{Cl}$/(RT) gives 2 S/m^2; iv) 220 x 10^{-6}/(7 x 10^{-4} x .054) gives 5.8 S/m^2
b) i) Unlike the previous example, we now have to consider the ratio of Cl concentrations, so $(j_{out}/j_{in}) = (c_{in}/c_{out}).\exp(- zFV_{oi}/RT)) = (1/0.2) \times \exp(-(-1) \times (-40/25)) = 5 \times 0.202 = 1.01$ The Cl influx is thus approximately the same as efflux, 0.53 μmol/m^2/s

Chapter 6

6.1 a) V_m = - 65 mV; R′ = 10^{6}Ω; C′ = 10^{-8} F. Time constant = R_mC_m = R′C′ = $10^6.10^{-8} = 10^{-2}$ sec.
(N.B. R′& C′ are in different units to those given on the sheet (R_m, C_m), but the product has the units of seconds in both cases).
b) $V = V_0.\exp(-t/\tau)$; so 5 (mV) = 10 (mV). exp(-t/10^{-2})
$(-t/10^{-2}) = \ln(5/10)$;
so t = 0.693 x 10^{-2} sec = 6.93 msec.

c) After 6.93 msec voltage has decayed to 5 mV, so a second depolarisation of 10 mV at that point in time gives a total depolarisation of 15 mV. Since the initial potential is -65 mV, a depolarisation of 15 mV brings the membrane potential to -40 mV, which therefore should be the threshold.

6.2   10 mV   0.489 mV
            .←   12 mm   →.

i) Space constant λ is given by eqn. $V = V_0\exp(-|x|/\lambda)$
        thus $\lambda = -|x|/(\ln(V/V_0))$
ii) $\lambda = - 12 \times 10^{-3}/(\ln(0.498/10)) = 4$ mm
iii) Time constant = R_mC_m = RC = 1 x 1.5 x 10^{-6} = 1.5 μs
(N.B. $R_mC_m = R/(2\pi a).2\pi aC = RC$)
iv) Intracellular resistance/ unit length

resistance of length l of axoplasm:

$R' = \rho_i l/(\pi a^2)$: $R'/l = R_i = \rho_i /(\pi a^2)$

v) $\lambda = \sqrt{[R_m/(R_i + R_o)]}$, and if we assume $R_o \ll R_i$, we can ignore R_o.

We are given $R = R_m .2\pi a = 1\Omega$; $\rho_i = R_i.\pi a^2 = 0.5$ Ω.m

10