WORKED ANSWERS

N.B. Where data from Tables in the texts have been used the values were originally calculated using the data from Silberberg. The calculated values will be close using the data from Brown, Le May & Bursten but they won't be exactly the same.

<u>UNITS AND GASES</u> ~ WORKED ANSWERS

(A) Descriptive Questions

1. (a) Concentration = amount of substance per given volume of solution units = mol m^{-3} (gases) or mol dm^{-3} (liquids, more common)

 $Mole-fraction of component = \frac{number of moles of component}{Total number of moles of all components present}$

Mole-fractions have no units.

2. Increasing the temperature increases the most probable speed and broadens the distribution of speeds of the molecules.



3. Ideal gases obey the classical gas laws (eg. pV = nRT) under all conditions of temperature and pressure.

(B) Calculations

1.
$$\sqrt{u^2} = \sqrt{\frac{3RT}{M}}$$

M for N₂ = 28.0 \therefore *M* = .0280 kg mol⁻¹

(the units for R and u require *M* in kg/mol)

R.M.S. velocity $(u_{rms}) = 4.000 \text{ x } 10^4 \text{ cm s}^{-1} = 4.000 \text{ x } 10^2 \text{ m s}^{-1}$

$$\therefore \qquad 4.000 \ge 10^2 \qquad = \sqrt{\frac{3 \ge 8.314 \ge T}{.028}}$$

$$\therefore$$
 T = **180K**

2.
$$\sqrt{\overline{u^2}}$$
 = root mean square velocity = $\sqrt{\frac{3RT}{M}}$

$$\therefore u_{rms} = \sqrt{\frac{3x8.314x273}{2.00x10^{-3}}}$$

$$=$$
 1.84 x 10³ m s⁻¹

3. Application of Graham's Law of Effusion

$$\frac{Rate(Sx)}{Rate(SO_2)} = 0.577 = \sqrt{\frac{M_r(SO_2)}{M_r(Sx)}} = \sqrt{\frac{64}{M_r(Sx)}}$$

$$\therefore \sqrt{M_r}(Sx) = \frac{8}{0.577} = 13.9$$

 $\therefore M_r(Sx) \triangleq 193$

Since atomic mass of S = 32. Must be S_6 at 500^0 C

At 860°C $1 = \frac{8}{\sqrt{M_r(Sx)}} \quad \therefore \quad M_r(Sx) = 64$ $\therefore \quad \underline{S_2} \text{ at 860°C}$ $4. \qquad \text{pV} = \text{nRT}$

rearrange n = pV/RT $n = 3.7 \times 1.013 \times 10^5 Pa \times 10.2 \times 10^{-3} m^3 / 8.314 Pa m^3 / mol K \times 500 K$ = 0.92 mol

5. This question makes use of pV = nRT

$$\label{eq:hard_states} \begin{split} n \ H_2 &= 0.174 \ g \ / \ 2.00 \ g \ mol^{-1} = 0.087 \ mol \\ nN_2 &= 1.365 \ g \ / \ 28.0 \ g \ mol^{-1} = 0.04875 \ mol \\ n_{total} &= 0.1358 \ mol \end{split}$$

 $x(H_2) = 0.64$ $x(N_2) = 1 - 0.64 = 0.36$

 $\begin{array}{ll} p_{total} &= n_{total} RT \ / \ V &= 0.1358 \ mol \ x \ 8.314 \ Pa \ m^3 \ / \ mol \ K \ x \ 273.15 \ K \ / \ 2.83 \ x \ 10^{-3} \ m^3 \\ &= 1.09 \ x \ 10^5 \ Pa \\ pH_2 &= ptotal \ x \ x(H_2) &= 1.09 \ x \ 10^5 \ Pa \ x \ 0.64 \ = 6.98 \ x \ 10^4 \ Pa \\ pN_2 &= ptotal \ x \ x(N_2) &= 1.09 \ x \ 10^5 \ Pa \ x \ 0.36 \ = 3.92 \ x \ 10^4 \ Pa \\ \end{array}$

6. $M_r(PCl_5) = 31 + 5x35.5 = 208.5$

We have $\frac{2.69}{208.5}$ mol PCl₅ initially = 0.0129 mol

 $PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$

0.0129 - *x x x*

At equilibrium total no. of moles present = $nPCl_5 + nPCl_3 + nCl_2$ = (0.0129 - x) + x + x= 0.0129 + x

We now find out the actual total number of moles present at equilibrium using the equilibrium pressure. pV = nRT

 $\therefore 1.0x1.013x10^5x1.0x10^{-3} = nx8.314x523$

:. n = 0.0233mol = 0.0129 + x:. x = 0.0104 mol $X(PCl_3) = X(Cl_2) = \frac{0.0104}{0.0233} = 0.446$ (these are the mole fractions X)

 $X(PCl_5) = 1 - (2 \times 0.446) = 0.108$

 $p(PCl_5) = 0.108 \times 1.013 \times 10^5$

 $= \underline{1.09 \times 10^4 Pa}$

 $p(PCl_3) = P(Cl_2) = .446x1..013x10^5$

 $= 4.52 \times 10^4 Pa$

COLLIGATIVE PROPERTIES ANSWERS

(A) Descriptive Questions

1. <u>Osmosis</u> is the diffusion of a solvent through a semipermeable membrane from a region of high solvent concentration to one of lower solvent concentration.

Osmotic Pressure is the pressure associated with the process of osmosis. It can be defined as the magnitude of the pressure that must be applied to the system (on the side of the membrane containing the lowest solvent concentration) which just prevents osmosis from occurring.

In <u>Reverse Osmosis</u> the solvent passes through a membrane from a region of low solvent concentration to one of higher concentration (e.g. from salt solution to pure water). This is achieved by applying a pressure on the low solvent concentration side of the membrane greater than the natural osmotic pressure of the system.

- 2. Because 0.1 mole of Na⁺Cl⁻ contains twice as many particles (ions in this case) as 0.1 mole of glucose (molecules in this case, glucose is a non-electrolyte). $\Delta T_{\rm f} = i K_{\rm b(solvent)} m_{\rm (solute)} \quad \text{here the } i \approx 2$
- 3. An ideal solution is one that obeys Raoult's Law at all concentrations.



1. We have
$$\frac{34.2}{342}$$
 mol (= 0.100 mol) of sucrose in 520 cm³ of solution

:. Concentration =
$$\frac{0.100}{520 \times 10^{-3}} mol \, dm^{-3} = 0.192 \text{ mol } dm^{-3}$$

We have $\frac{34.2}{342}$ mol of sucrose in 500 g H₂O.

 \therefore Molality (amount of sucrose/kg solvent) = 0.100 / 0.500

$= 0.200 \text{ mol kg}^{-1}$

We have 0.100 mol of sucrose in $(500g / 18.0 g \text{ mol}^{-1}) \text{ mol } H_2O$

	· Mole frac	rtion v(si	icrose) –	$-\frac{0.100}{-0.0036}$
	While frac		ucrosc) =	$-0.100 + \frac{500}{2}$
				18.0
	\therefore x(water) =	= 1.00000)00359	9 = 0.9964
	π	= [sucro = [0.192	ose]RT mol/L] or [0.192	0.0821 atm L / K mol 293.15K 2 mol/L x 10 ³ mol/m ³] {8.314 Pa m ³ / K mol) /1.0133x10 ⁵ } 293.15K
		= 4.62	atm	$= -\psi_{\pi}$ (osmotic potential)
The water	r potential is	Ψ	=	$ \psi_{\pi} + \psi_{p} $ -4.62 + 0 (pressure potential is zero)
2.	$\Delta T = K_F x m$		m = mol	lality of solute (mol / kg solvent)
T ₂ - T ₁ ∴ 5.7 -	$= K \ge m$ 1.1 = 7.00 \x m			
∴ <i>m</i> =	$=$ $\frac{4.6}{7.00}$			
=	= 0.657 mol / kg	solvent		Take molar mass of unknown as M g mol ⁻¹
∴ Solut	tion as made up h	nas		$\frac{2.05 \times 1000}{M \times 40.0}$ mol/kg nitrobenzene
	$\therefore 0.657 = \frac{2.0}{M}$	05 x 1000 (x 40.0)	
	$\therefore M = 78 \text{ g mo}$	\mathbf{h}^{-1}		
	∴ M.W. unknov	vn = 78		
3. 1	Formula ratio of a	atoms =		$\frac{18.3}{12}C:\frac{0.51}{1}H:\frac{81.2}{79.9}Br$
			i.e. 1.5 (C: 0.5H: ~1 Br
			∴ Empir	rical Formula = $(C_3H_1Br_2)_n$
2	$\Delta T_{\rm B} = i {\rm x} {\rm K}_{\rm B} {\rm x} {\rm x}$	m		Take $i = 1$ (assume a non-electrolyte)
	$\therefore 0.33 = 3.63$	x m		\therefore m = 0.0909 mol/kg solvent
Have 0.79	93 g of cmpd in 0).01480 d	m ³ of CH	$HCl_3 (\rho = 1.485 \text{ kg dm}^{-3})$
		1 100 1		

: 0.793 g of cmpd in (0.01480 x 1.485) kg of CHCl₃

$$\Rightarrow \frac{0.793}{0.0148 \times 1.485} \text{ g of cmpd in } 1 \text{ kg of CHCl}_3$$

Let molar mass of cmpd = M g mol⁻¹

 $\therefore \text{Have} \frac{0.793}{0.0148 \text{ x } 1.485 \text{ x } M} \text{ moles of cmpd in 1 kg of CHCl}_{3}$

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This number of moles = 0.0909 (see above)

$$\therefore M = \frac{0.793}{0.0148 \text{ x } 1.485 \text{ x } 0.0909} = 397 \text{ g mol}^{-1}$$

i = 1

M.W. = 397

Formula weight $C_3H_1Br_2 = 197$

 $\therefore n = 2$ (in empirical formula)

Molecular Formula = $C_6H_2Br_4$

4. $\pi = i[c]RT$

(proteins are non-electrolytes)

- ∴ $6255 = [c] \times 8.314 \times 298$ ∴ $[c] = 2.525 \text{ mol m}^{-3}$ Have 1.50g in 0.1 dm³
- $\therefore 1.50 \text{ g in } 10^{-4} \text{ m}^3$
- $= 1.5 \text{ x } 10^4 \text{ g in } 1 \text{ m}^3$

Take molar mass of albumin as $M \text{ g mol}^{-1}$

 $\{[c] = n / V = (g / M) / V\}$

$$\therefore [c] = \frac{1.5 \times 10^4}{M} \mod m^{-3} = 2.525 \mod m^{-3}$$
(see above)

$$\therefore M = \frac{1.5 \times 10^4}{2.525} = 5940 \ g \ mol^{-1}$$

$$\therefore M.W. = 5940$$
5. $\Delta T_F = i \times K_F \times m$ $BaCl_2 \rightarrow Ba^{2+} + 2Cl^{-1}$
 $\therefore i \equiv 3$ (this is an electrolyte which behaves as above)
 $\equiv 3 \times 1.865 \times 0.1$
 $\equiv 0.56^{\circ}C$ (this is the change in temperature)
 $\therefore f.p. = -0.56^{\circ}C$
6. $sucrose = C_{12}H_{22}O_{11}$ $M_{sucrose} = 342.3 \ g/mol$
[sucrose] $= 34.2 \ g/L / 342.3 \ g/mol$
 $= 9.99 \times 10^{-2} \ mol/L$
 $\pi = i[sucrose]RT$
 $= 1 \times [9.99 \times 10^{-2} mol/L] \ 0.0821 \ atm \ L / K \ mol 293.15K \ or [9.99 \times 10^{-2} \times 10^{3} \ mol/m^{3}] \{8.314 \ Pa \ m^{3} / K \ mol / 1.0133 \times 10^{5}\} 293.15K$
 $= 2.40 \ atm$

As this is reverse osmosis then a pressure exceeding 2.40atm must be applied to the side of the membrane that contains the sugar solution so that water is transferred to the side of the membrane that is pure water.

CHEMICAL KINETICS ANSWERS

Section A

- 1. Mix the reactants at constant temperature and then determine the concentration of one of them (or alternatively, product) as a function of time. [It is usually best to monitor the concentration change by a physical technique, i.e. measure some physical property of the system that is changing and can be related to a concentration reactant or product.]
- 2. The <u>order</u> of a chemical reaction is the sum of the concentration exponents in the differential rate expression from the reaction. Thus, if the reaction rate involving two reactants A and B is given by:

$$\frac{-d[A]}{dt}\left(\operatorname{or}\frac{-d[B]}{dt}\right) = k[A]^{x}[B]^{y},$$

The reaction order (overall) is x + y. The reaction is also described as x order with respect to [A], yet order w.r.t. [B]. (Note that the order of a reaction is not necessarily an integer.)

The <u>molecularity</u> of a reaction is a term that can be applied only to an elementary (i.e. one step) reaction. (Of course, a number of elementary reactions constitute every complex, i.e. multiple step, reaction).

It is the number of reacting species involved in the elementary reaction,

e.g.'s			
A	\rightarrow	Unimolecular	(common)
A + B	\rightarrow	Bimolecular	(very common)
A + B + C	\rightarrow	Termolecular	(rare)
A + B + C + D	\rightarrow		(No case known)

3. In general the rate of mean reaction will be given by the expression:

$$\frac{-d[A]}{dt} = k[A]^{x}[B]^{y}$$

Where A and B are the two reactants, x + y is the reaction order and k is the rate constant. These can be evaluated by using one of two possible approaches:

<u>Either</u>

(i) Add one reagent, say B, in large excess - the above equation now simplifies to:

$$\frac{-d[A]}{dt} = k'[A]^x \quad \text{where } \mathbf{k}' = \mathbf{k}[\mathbf{B}]^{\mathbf{y}}.$$

Measure [A] (by a physical or chemical method) at different time intervals keeping the temperature of the reaction mixture constant. Plot the data according to the various integrated rate equations for one reactant and determine which one gives a good straight line fit. This will identify x, i.e. the order with respect to [A] (e.g. if a plot of ln [A] v time is a straight line, x = 1). [N.B. for this procedure the reaction should be followed until at least 75% of A has disappeared]. From the slope of the straight line plot k' is evaluated.

The reaction is now repeated with A in excess and [B] measured as a function of time. The data obtained is analysed to the same procedure as described above and *y* evaluated. In the expression $k' = k[B]^y$, k' and *y* are now known and [B] is the known excess concentration of B that was used in the first experiment, k can therefore be evaluated.

<u>OR</u>

- (ii) At constant temperature measure the initial rate of the reaction in a series of experiments where the initial concentration of B, [B₀], is kept constant and the initial concentration of A, [A₀], is varied.
- \therefore Initial Reaction Rate = $k[A_o]^x [B_o]^y$

 $= k'[A \circ]^x$ where $k' = k[B \circ]^y$

- Examine how the initial rate depends on $[A_0]$ and thereby identify *x*. This procedure will also evaluate k' (as we know the initial rate at a particular $[A_0]$.
- Now repeat the above procedure keeping [A $_0$] constant and varying [B $_0$]. Analysis of this data will give *y* and hence *k*. [The initial rate of a reaction is determined by accurately measuring the concentration of a reactant (or product) at different times close to the start of the reaction if possible within the first 5% of reaction. From the plot of concentration v time the initial rate is determined by measuring the tangent at zero time.
- 4. Because as temperature increases the fraction of molecules present with kinetic energy $\geq E_a$, the activation energy, of the reaction increases. The activation energy of a reaction is the kinetic energy colliding molecules require to enable them to pass through the transition state of the reaction and form products:



Reaction coordinate

As a consequence, as the temperature increases a greater proportion of molecular collisions will result in chemical reaction:



[N.B. As the temperature increases the rate of collision, Z_{AB1} increases. However, this effect is $\propto T^{\frac{1}{2}}$ and has a much smaller influence on the reaction rate than the effect described above.]

The rate of reaction a typical biomolecular reaction is expressed in the equation $Rate = k[A]^{x}[B]^{y}$ The rate constant k is therefore proportional to the rate of reaction. The temperature dependence of the rate constant is expressed in the Arrenhius equation: $k = A e^{-Ea/RT}$ where k = rate constant, A = frequency factor, R = gas constant, T = temperature The form of this equation indicates that the large the temperature the larger the value of the rate constant (even if E_a were to stay constant).

5. Measure the rate constant of the reaction at different temperatures and then plot the data as below



The pre-exponential factor A is determined from the intercept on the y axis (In A) where

6. By modifying the reaction mechanism so that the activation energy of the reaction is reduced.



(B). Calculations

1. The reaction is first order so the form of the integrated rate equation we use is:

 $\therefore \ln[A_o] - \ln[A] = kt$

 $[A_o]$ = initial concentration; [A] = concentration at time t

We need to calculate *t* for [A] to fall to

 $\therefore \ln[\operatorname{Ao}] - \ln ([\operatorname{Ao}]/10) = k t_{9/10}$ (using the laws of logs) $t_{9/10} = \frac{\ln 10}{k} = \frac{2.303}{5x10^{-4}} \sec$ $= 4.6 \times 10^3 \mathrm{s}$

[Ao]

10

2. $ln[A_o] - ln[A] = kt$

 $\ln[A] - \ln[A_o] = -kt$ (rearrange so that we have the fraction remaining $[A]/[A_o]$

$$\therefore \ln([A]/[A_0]) = -2.08 \times 10^{-6} \times (3.38 \times 24 \times 60 \times 60)$$

= - 0.6074

$$\therefore [A]/[A_o] = 0.545 \quad (taking inverse ln of both sides)$$
This is fraction of radon remaining

3. $\ln[A_o] - \ln[A] = kt$

When 99% of element has disintegrated we have 1% left.

$$\therefore \ln(1) = -kt_{99\%} + \ln(100) \qquad (1\% = [A], 100\% = [A_0])$$

$$t_{99\%} = \frac{\ln(\frac{100}{1})}{k} = \frac{\ln(100)}{2.31 \times 10^{-7}} yr$$

$$= 1.99 \times 10^7 yr$$

= **1.99** x **10**⁷ years

4. If reaction is 1st order then it obeys the equation:

 $ln[A_o] - ln[A] = kt$

 $t_{1/2} t_{1/2} t_{1/2}$ is time for half reaction to occur, i.e. $t = t_{1/2}$ when [A] = [A₀]/2

$$\therefore \ln [Ao] - \ln \left(\frac{[Ao]}{2}\right) = kt_{\frac{1}{2}}$$

$$\therefore \ln [Ao] - \{ \ln [Ao] - \ln(2) \} = kt_{1/2}$$

$$\therefore k = \ln(2) / t1/2 = \ln(2) / 53 \text{ x } 60 \text{ sec}^{-1} = 2.18 \text{ x } 10^{-4} \text{ s}^{-1}$$

60)

Now we look at the second set of conditions to check that the equation is being obeyed.

$$\ln(100) - \ln(27) = k \ge (100 \ge 100)$$
$$\therefore k = \frac{\ln\left(\frac{100}{27}\right)}{100 \ge 60} = \frac{1.309}{6000}$$
$$= 2.18 \ge 10^{-4} \text{ s}^{-1}$$

Since the two separately calculated k values are the same, the reaction must be first order with $k = 2.18 \times 10^{-4} s^{-1}$

5. k = $A e^{-Ea/RT}$

 $\ln k = \ln A - Ea / RT$ (taking ln of both sides)

case (A) $\ln(5.03 \times 10^{-2}) = \frac{E}{R \times 298}$

case (B) $\ln(6.71) = \frac{E}{R \ge 333}$

$$\therefore \qquad \ln\frac{(5.03 \times 10^{-2})}{6.71} = -\frac{Ea}{R} \left(\frac{1}{298} - \frac{1}{333}\right) \qquad \text{taking (B) from (A)}$$

 $Ea = 115437 \text{ J mol}^{-1} = 115 \text{ kJ mol}^{-1}$

Recall the general form is:

$$\ln\!\left(\frac{k_2}{k_1}\right) = -\frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substitute Ea determined with and rearrange

$$k_2 = k_1 x e \{ -\frac{Ea}{R} (\frac{1}{T_2} - \frac{1}{T_1}) \}$$

$$k_2 = 6.71 \,\mathrm{x} \, e\{-\frac{115 \,\mathrm{x} \, 10^3}{8.314} (\frac{1}{305} - \frac{1}{333})\}$$

above gives k at 305K as 1.5 x 10⁻¹ dm³mol⁻¹s⁻¹

6. From experiments 1 and 2, doubling $[BrO_3^-]$ at constant $[Br^-]$ and $[H^+]$ doubles rate.

 \therefore rate \propto [BrO3⁻]

From experiments 1 and 3 increasing [Br] by factor of 3 at constant $[BrO_3]$ and $[H^+]$ increases reaction rate by factor of 3

 \therefore rate \propto [Br⁻].

From experiments 2 and 4 increasing [H⁺] by factor of 3/2 at constant

[BrO₃⁻] and [Br⁻] increases reaction rate by

 $\frac{5.4}{2.4} = 2.25$ times.

Since

$$\left(\frac{3}{2}\right)^2 = 2.25$$
, then rate $\propto \left[\mathrm{H}^+\right]^2$

 \therefore Reaction Rate = k[BrO₃⁻][Br⁻][H⁺]²

and the reaction is overall fourth order.

THERMOCHEMISTRY ANSWERS

1. <u>Extensive properties</u> depend on the amount of a substance being considered, e.g. Volume (V), energy (E), enthalpy(H), entropy(S), free energy(G).

<u>Intensive properties</u> are independent of the amount of substance being considered, e.g. pressure(p), temperature(T), density(ρ).

<u>State properties</u> have fixed values when a system is at equilibrium. When a change in state occurs, changes in state properties are given by the value in the final state minus the value in the initial state, and are thus *independent of the pathway* in moving from State 1 \longrightarrow State 2, e.g. pressure (p), enthalpy (H):

 $\Delta \mathbf{p} = \mathbf{p}_2 - \mathbf{p}_1, \Delta \mathbf{H} = \mathbf{H}_2 - \mathbf{H}_1$

<u>Path properties</u> are only associated with changes in the state of a system. The value of these *depend on the pathway* taken between the initial and final states,

e.g. work (w), heat (q) State 1 \longrightarrow State 2 route \uparrow

The value of w and q depend on the route taken in going from State 1 to State 2.

The <u>Internal Energy (E)</u> of a system is the sum over all molecules in the system of the values of the different forms of energy possessed by the molecules.

$$E = \sum_{all.molecules}^{over} E_{thermal} + E_P$$

=
$$\sum_{all.molecules}^{over} (Translational E + Rotational E + Vibrational E) + (Atomic E + Bond E + Nuclear E)$$

The enthalpy (H) of a system is its energy plus the product of its pressure and volume,

i.e. H = E + pV

<u>Bond Energy (B.E.)</u> is the average energy required to break a particular bond in 1 mole of a substance in the gas phase.

A substance is in its standard state if it is pure and in its most stable form at 1 atmosphere pressure.

<u>Standard Enthalpy (H⁰</u>) is the enthalpy of a substance when it is at 1 atmosphere pressure and in its most stable form.

<u>Energy changes</u> are evaluated by determining the heat of reaction measured at constant volume ($\Delta E = q_V$).

<u>Enthalpy changes</u> are evaluated by determining the heat of the reaction measured at constant pressure ($\Delta H = q_p$).



The labelled diagram above summarises the essential features of Bomb Calorimeter.

The sample is ignited (by passing a small current momentarily through the electrical wire which is placed near sample surface in the Pt crucible – not shown in the above diagram). The amount of heat liberated is calculated from the rise in temperature of the surrounding water. We need to know the heat / water equivalent of the bomb. This calibration step is usually done by first burning a compound whose heat of combustion is known in the bomb.

Note that heats of combustion are measured <u>under constant volume</u> (not constant pressure) conditions. Thus ΔE_c is measured.

Thus a bomb calorimeter is used to determine the heat of reaction which is then converted to ΔH^o_c by use of the equation $\Delta H^o_c = \Delta E^o_c + \Delta n_g RT$.

- 2. (a) Entropy (S) is an energetic term which is a measure of the molecular disorder of a system. (i.e. the number of ways the energy of a system can be distributed among the molecules.) The units of S are J K^{-1} .
 - (b) The Free Energy (G) of a system is a measure of its potential to undergo physical or chemical change. The units of G are J.

G for a system or a substance is defined by:





 ΔG is a quantitative evaluation of the enthalpy and entropy driving forces for a change in state of a system.

If ΔG is –ve, the change will be spontaneous. If ΔG is +ve, the change will not occur.

3. These answers have been calculated with slightly different values for the input data. Your results should be very close.

(a)
$$C_2H_6(g) + 7/2 O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$$

-84.6670 2 x -393.5 3 x -285.84
 $\Delta H^0 = (2 x - 393.5 + 3 x - 285.84) + 84.667$
= -1559.9kJ

$$\therefore \qquad \Delta H_{c}^{o} (C_{2}H_{6}g,298K) = -1559.9 \text{ kJ mol}^{-1}$$

(b)
$$2NH_3(g) + 5/2 O_2(g) \rightarrow 3H_2O(g) + 2NO(g)$$

 $2x - 45.9 0 \qquad 3x - 241.826 \qquad 2x 90.29$

$$\Delta H^{\circ} = (3 x - 241.826 + 2 x 90.29) + 2 x 45.9$$

= -453.098

 $\therefore \Delta H_{c}^{o}(NH_{3}, g, 298K) = -226.5 \text{ kJ mol}^{-1} (N.B. \Delta H_{c}^{o} \text{ is for 1 mole of reactant})$

(c)

$$H \longrightarrow H (g) \rightarrow N(g) + 3H(g)$$

$$-45.9 \qquad 473.0 \quad 3 \ge 218.0$$

$$\Delta H^{\circ} = (473.0 + 3 \ge 218.0) + 45.9$$

$$= 1172.9 \text{ kJ}$$

$$\therefore N - H \text{ bond energy} = 1172.9 / 3 = 391 \text{ kJ mol}^{-1}$$
(N.B. there are 3 NH bonds)
(d)
$$CS_{2}(l) + 3O_{2}(g) \rightarrow CO_{2}(g) + 2SO_{2}(g)$$

$$87.9 \qquad 0 \qquad -393.5 \qquad 2 \ge -296.8$$

	$\Delta H^{\rm o}$		=	(-393.5	- 2 x 2	96.8) - 87	7.9 = -	-1075.0	kJ mol ⁻¹	
	$\therefore \Delta H^{o}_{c}$	$(CS_{2,\ell},2)$	98K)	= -107	5.0 kJ m	ol ⁻¹				
(e)	SO ₂ (g) -296.8	+ 1/2 C	$D_2(g) + 0$	H ₂ O(g) -241.8	\rightarrow 26	$H_2SO_4(\ell)$ -8	313.989)		
	$\therefore \Delta H^o$		=	-813.98	89 + (24	1.826 + 2	296.8)			
			=	-275.4	kJ					
(f)	<i>(i)</i>	NH ₃ (g) -45.9		\rightarrow	1/2 N ₂ (§ 0	g) +	3/2 H	$_{2}^{2}(g)$		
	$\therefore \Delta H^o$		=	45.9 k.	J					
	(ii)	$2H_2S(g)$ 2 x -20) + 3O ₂ .2	$ \begin{pmatrix} g \\ 0 \end{pmatrix} $	\rightarrow	2H ₂ O(l) 2 x -285.8	84	+	2SO ₂ (g) 2 x -296.8	
	$\therefore \Delta H^o$		=	(2 x –2	85.84 -	2 x 296.8)	+ 2 >	x 20.2		
			=	-1124.9	kJ					
(g)	H-O-H(-241.82	(g) 26	\rightarrow	2H(g) 2 x 218	+	O(g) 249.2				
	$\Delta H^{\rm o}$		=	(2 x 21	8 + 249	9.2) + 241	.826			
			=	927.0 k	J					
	∴O-H	bond ene	ergy	=	927.0 /	2		= 464	kJ mol ⁻¹	
4.	Ba(s) +	- ¹ ∕2O₂(g	.)		BaO(s)					

$Ba(s) + \frac{1}{2}O_2(g)$	BaO(s)
ΔS = -ve as there is ordered solution	lid on the RHS whereas there is solid and gas on the LHS
the system becomes more ordered	ed entropy decreases
$BaCO_3(s)$	$BaO(s) + CO_2(g)$
$\Delta S = +ve$ as there is ordered so	lid on the LHS whereas there is solid and gas on the RHS
the system becomes less ordered	and entropy increases
$Br_2(g)$	2Br(g)
$\Delta S = +ve$ as we go from 1 mole	e of gas on the LHS to 2 moles of gas on RHS
the system becomes less ordered	l (more molecules) and entropy increases
$H_2(g) + Br_2(I)$	2HBr(g)
$\Delta S = +ve$ as we go from 2 mo	blecules of gas + liquid LHS to 2 molecules of gas RHS we increase
the disorder of the system and se	o the entropy increases.

5.

(a)
$$2C (graphite) + 2H_2(g) \rightarrow C_2H_4(g)$$

0 0 68.36 6.

 ΔG^{o} = 68.36 kJ Non-spontaneous at 298 K (b) 2C $+ 3H_2(g)$ $C_2H_6(g)$ \rightarrow 0 0 -32.89 ΔG° = -32.89 kJ Spontaneous at 298 K 3CuO(s) + 2Al(s) $Al_2O_3(s) + 3Cu$ \rightarrow 3 x - 130 + 0-1582 0 ΔG° = -1582 + 390= -1192 kJ (-1198 Zumdahl) reaction is spontaneous -ve .:. 3CaO(s) + 2Al(s) \rightarrow $Al_2O_3(s) + 3Ca$ 3 x -603.5 0 -1582 0 ΔG° = -1582 + 1810.5= 228.5 kJ reaction is non-spontaneous, CaO cannot be reduced by Al metal. *:*. +ve

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ 7.

> $\Delta H^{\circ} = (2x-395.2) - (2x-296.9) = -196.6 \text{ kJ/mol}$ $\Delta S^{\circ} = (2x256.2) - (2x248.5 + 205.0) = -189.6 \text{ J/mol K}$

 ΔG^{o} $= \Delta H^{\circ} - T \Delta S^{\circ}$ $= -196.6 - 298 \text{ x} - 189.6 \text{ x} 10^{-3} \text{ kJ/mol}$ = -140.1 kJ; spontaneous

CHEMICAL EQUILIBRIUM ANSWERS



At equilibrium 40% of PCI₅ had dissociated $x = 40/100 * 2 / 2 = 0.4 \text{ mol dm}^{-3}$ Amount of PCI₅ remaining = 0.6 mol dm⁻³

$$K_{c} = \frac{\left[PCl_{3}\right]\left[Cl_{2}\right]}{\left[PCl_{5}\right]} = \frac{0.4mol\,dm^{-3}\,x0.4mol\,dm^{-3}}{0.6mol\,dm^{-3}}$$
$$= 2.66\,x\,10^{-1}\,\text{mol}\,dm^{-3}$$

3.

(i)

$$K_p = p_{SO2} x p_{SO3}$$
 (N.B. Solid phases do not appear in this equation.)

Since all SO_2 and SO_4 is formed from $FeSO_4$

4.
$$Fe_2O_3(s) + H_2(g) = 2FeO(s) + H_2O(g) \Delta G^{\circ}(298K) = +31 \text{ kJ}$$

5.

 ΔG° -RT x lnK = ∴ + 31000 = -8.314 x 298 x lnK e(-31000/8.314 x 298) = Κ Hence K 3.7 x 10⁻⁶ = K_p for reaction = pH_2O pH_2 $K_p = (p^o)^{\Delta n} K$ here $\Delta n = \text{products} - \text{reactants} = 1 - 1$ = 0 K_p [as $(p^o)^0 = 1$] In this case therefore Κ = 3.7 x 10⁻⁶ $\therefore K_p =$ CaCO₃(s) ⇆ CaO(s) + $CO_2(g)$ -603.5 -394.4 -1128.8 ΔG° - 603.5 - 394.4 + 1128.8 = 130.9 kJ = ΔG° = -RT x lnK \therefore 130.9 x 10³ = -8.314 x 298 x lnK $\therefore K^{o}$ = $e(-130.9 \times 10^3 / 8.314 \times 298) =$ e(-52.834) 1.13 x 10⁻²³ = $\therefore K^{o}$

This value equals numerical value of K_p when the latter has units of atm

For above reaction $K_p = (pCO_2)$

$$K_{p} = (p^{o})^{\Delta n} K \qquad \Delta n = 1$$

= (1.0135 x 10⁵)¹ x K^o
∴ K_p = (pCO₂)_{equilibrium} = 1.4 x 10⁻²³ atm
(pCO₂)_{equilibrium} = **1.1 x 10⁻¹⁸ Pa**

6. Relevant equation:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\therefore \ln\left(\frac{K_2}{4.6 \,\mathrm{x} \,10^{-31}}\right) = -\frac{180.5 \,\mathrm{x} \,10^3 \,\mathrm{x}}{8.314} \left(\frac{1}{2400} - \frac{1}{298}\right)$$

$$\frac{-1}{1.6 \times 10^{-31}} = 63.81$$

$$\therefore \frac{K_2}{4.6 \,\mathrm{x} \, 10^{-31}} = 5.156 \,\mathrm{x} \, 10^{27}$$

(inverse *ln* of both sides)

 $\therefore K_2 = 2.4 \times 10^{-3}$

ELECTROCHEMICAL CELLS ~ ANSWERS

(A) Descriptive Questions

 Sketch the glass electrode used to measure pH indicating its essential features. Briefly discuss the mode of operation of this electrode. What is the relationship between the potential developed by this electrode (relative to some reference electrode) and the pH of the solution?



Electrode potential of glass electrode depends on $[H_3O^+]$ of solution in which it is placed.

 $(E_{glass} = k + 0.059 \log_{10}[H_3O^+]$ where k value varies from day to day.) If another electrode (e.g. calomel electrode) is placed in the solution whose electrode potential does not depend on pH, the resulting electrochemical cell can be represented by:

glass	solution	calomel electrode
electrode		

Thus $E_{cell} = E_{calomel} - E_{glass} = E_{calomel} - k + 0.059 pH$

 $E_{calomel}$ is known, k is evaluated by measuring E_{cell} for solution of known pH; hence evaluation of E_{cell} with a solution of unknown pH allows the later value to be determined.

- 2. Outline the chief features of
- (a) A calomel electrode is an example of a metal-insoluble salt-anion electrode or half-cell. It essentially consists of a mixture of mercury and mercurous chloride (calomel) in contact with a solution containing a fixed concentration of chloride ions.

$$Hg_{(1)}$$
 Hg_2Cl_2 Cl^-

(b) Standard Hydrogen Electrode



Hydrogen gas at 1 atmosphere (unit pressure) is adsorbed at the surface of the electrode in contact with a solution containing H_3O^+ at unit concentration ($[H_3O^+] \cong 1 \mod \text{dm}^{-3}$).

(B) Calculations

For the reaction $Cu(s) + 2AgCl(s) \rightarrow 2Ag(s) + Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{n \, x \, F} \ln \left(\frac{[Ag(s)]^2 \, x [Cu^{2+}(aq)] x [Cl^{-}(aq)]^2}{[Cu(s)] x [AgCl(s)]^2} \right)$$

$$\therefore 0.030 = -0.117 - \frac{8.314 \, x \, 298}{2 \, x \, 96500} \ln \left\{ \frac{1 \, x [Cu^{2+}(aq)] \, x \, 0.1^2}{1 \, x \, 1^2} \right\}$$

 $\therefore 0.030 = -0.117 - 0.01284 \ln\{[Cu^{2+}]x[0.01]\}\$

$$\therefore 0.147 = -0.01284 \ln[Cu^{2+}_{(aq)}] - 0.01284 \ln[0.01]\}$$

$$\therefore 0.147 = -0.01284 \ln[Cu^{2+}_{(aq)}] + 0.0591$$

$$\therefore -(\frac{0.147 - 0.0591}{0.01284}) = \ln [Cu^{2+}_{(aq)}]$$

- \therefore -6.8458 = ln[Cu²⁺_(aq)]
- $\therefore \exp(-6.8458) = [Cu^{2+}_{(aq)}]$

Hence $[Cu^{2+}] = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$

2.

$$\frac{2\operatorname{Fe}^{3\pm} + 2e \rightarrow 2\operatorname{Fe}^{2\pm}}{\operatorname{Sn}(s) + 2\operatorname{Fe}^{3+}(aq) \rightarrow 2\operatorname{Fe}^{2+}(aq) + \operatorname{Sn}^{2+}(aq)}$$

 $\underline{Sn(s) + 2Fe^{3+}(aq)} \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{2F} ln \left\{ \frac{\left[Fe^{2^{+}}\right]^{2} x \left[Sn^{2^{+}}\right]}{\left[Sn\right] x \left[Fe^{3^{+}}\right]^{2}} \right\} \qquad Fe(SO_{4}) \rightarrow Fe^{2^{+}} + SO_{4}^{2^{-}}}{0.1 \qquad 0.1 \qquad 0.1$$

3.

Zn(s)	Zn ²⁺ (aq)	sea	AgCl(s)	Ag(s)
m 0	· · · ·	1	I	1

$$c = 0.01M$$

$$Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

$$2AgCl(s) + 2e^{-} \rightarrow 2Ag(s) + 2Cl^{-}_{(aq)}$$

Cell Reaction:
$$\underline{Zn}(s) + 2\underline{AgCl}(s) \rightarrow \underline{Zn}^{2+}_{(aq)} + 2\underline{Cl}^{-}_{(aq)} + 2\underline{Ag}(s)$$

$$\Delta G^{\circ} = -n F E^{\circ}_{cell} = -n F (E^{\circ}_{cathode} - E^{\circ}_{anode})$$
$$= -2 x 96500 x (0.223 - -0.761)$$
$$= -2 x 96500 x 0.984J$$

= -190 kJ

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nxF} \ln \left(\frac{[Zn(aq)^{2+}]x[Cl(aq)^{-}]^2x[Ag(s)]^2}{[Zn(s)]x[AgCl(s)]^2} \right)$$

$$\therefore 1.059 = E_{cell}^{\circ} - \frac{8.314 \times 298}{2x96500} \ln \left\{ \frac{0.01 \times [Cl^{-}]^2 \times 1^2}{1 \times 1^2} \right\}$$

$$\therefore 1.059 = 0.984 - \frac{2477.572}{193000} \ln\{[0.01][C1^{-}]^{2}\}$$

 $\therefore 1.059 = 0.984 - \{(0.01284) \ ln[Cl^{-}]^{2} + 0.01284 \ ln[0.01]\}$

 $\therefore 1.059 = 0.984 - (0.01284 \text{ x } 2) ln[Cl^{-}] + 0.059$ (if you have problems with this see BLB Appendix A.2 Logarithms)

 $\therefore 1.059 = 0.984 - 0.02567 \ln[\text{Cl}^-] + 0.059$

 $-(0.016/0.02567) = ln[Cl^{-}]$

Hence $[CI^{-}] = 0.536 \text{ mol dm}^{-3}$



$$Cu(s) \rightarrow Cu^{2+} + 2e^{-}$$

HgO(s) + H₂O + 2e⁻ \rightarrow Hg(l) + 2OH

Cell Reaction: $\underline{Cu(s) + HgO(s) + H_2O(l) \rightarrow Hg(l) + 2OH^{\underline{-}}(aq) + Cu^{\underline{2+}}(aq)}$

N.B. The following working makes use of the alternative form of the Nernst equation using log_{10} instead of *ln*. You can solve the problem just as easily (probably more easily!) using the *ln* form of the equation.

 $E^{o}_{cell} = 0.098 - 0.34 V$

$$= -0.242 \text{ V}$$

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{2xF} \log_{10} \left(\frac{[Hg]x[OH^{-}]^{2}x[Cu^{2+}]}{[Cu]x[HgO]x[H_{2}O]} \right)$$

$$\therefore 0.112 = -0.242 - \frac{0.0592}{2} \log_{10} \left(\frac{1x[OH^{-}]^{2}x0.01}{1x1x1} \right)$$

$$0.354 = -\frac{0.059}{2} \log_{10} \left(\frac{[OH^{-}]^{2}}{100} \right)$$

$$-12.0 = \log_{10} \left(\frac{[OH^{-}]^{2}}{100} \right)$$

$$-12 = (2 x \log_{10}[OH^{-}]) - 2 \qquad (NB: \log(A/B) = \log A - \log B \log_{10}[OH^{-}]) = 2\log_{10}[OH^{-}])$$

$$\therefore 12 = -(2 x \log_{10}[OH^{-}]) + 2 \qquad (multiplied both sides by -1)$$

$$\therefore 10 = 2 x pOH$$

$$\therefore pOH = 5.00$$

$$[OH^{-}] = 1 x 10^{-5} M$$

pH = 14.0 - 5.00 = 9

ACID~BASE EQUILIBRIA ~ WORKED ANSWERS

 $H_2SO_4 + H_2O$ $HSO_4^- + H_3O^+$ 1. H_2SO_4 \rightarrow $NH_3 + H_3O^+$ $NH_4^+ + H_2O$ NH₄CI ⇆ Decreasing acid strength KNO₃ **Neutral Solution** NaCN $CN^{-} + H_2O$ ⇆ $HCN + OH^{-}$ NaNH₂ $NH_{2}^{-} + H_{2}O$ $NH_3 + OH^ \rightarrow$

= 1.30

- (a) $\operatorname{HCl} + \operatorname{H}_2 0 \longrightarrow \operatorname{H}_3 O^+ + \operatorname{Cl}^- 0.050 0.050$
- (b) $K^+OH^- + H_2O \rightarrow OH^-(aq) + K^+(aq) = 0.030$

 $pOH = -log_{10} 0.030 = 1.52$

 $pH = -log_{10} 0.050$

(c) $HCOOH + H_2O$ \Leftrightarrow $H_3O^+ + HCOO^-$.001 - x x x

$$K_A = \frac{[H_3O^+][OH^-]}{[HCOOH]}$$

$$1.8 \,\mathrm{x} \, 10^{-4} = \frac{x^2}{0.001 - x}$$

Now 0.001 >> 1.8 x 10^{-2} (i.e. 100 x K_A) \therefore cannot approximate.

We must solve the quadratic equation.

$$1.8 \ge 10^{-7} - 1.8 \ge 10^{-4} \ge x^2$$

 $\therefore x^{2} + 1.8 \ge 10^{-4} x - 1.8 \ge 10^{-7} = 0$ This is now in the usual form $0 = ax^{2} + bx + c$: $a = 1, b = 1.8 \ge 10^{-4}, c = -1.8 \ge 10^{-7}$

To solve we use : $x = [-b + \sqrt{b^2 - 4ac}] / 2a$

and
$$x = \frac{-1.8 \times 10^{-4} \pm \left[1.8^2 \times 10^{-8} + 4 \times 1 \times 1.8 \times 10^{-7}\right]^{\frac{1}{2}}}{2 \times 1}$$

- Taking the +ve solution $x = 3.44 \times 10^{-4}$ [H⁺] = 3.44 x 10⁻⁴ mol dm⁻³
- $\therefore pH = -log_{10}[H^+] = 3.46$
- (d) HCN + H₂O \leftrightarrows H₃O⁺ + CN⁻ 1.0 - x x x

$$\therefore 4.8 \,\mathrm{x} \, 10^{-10} = \frac{x^2}{1.0 - x}$$

Now 1.0 >> 4.8 x 10⁻⁸ (1.0 >> 100 x K_A) and \therefore we can approximate

$$\therefore x = [H^+] = \sqrt{[HA]}K_A = \sqrt{1.0 \times 4.8 \times 10^{-10}}$$

$$\therefore pH = -\log_{10}[H^+] = 4.66$$

(e) Ammonium chloride is a salt and is fully ionised in solution.

$$\begin{array}{ccc} \mathrm{NH_4Cl} & \rightarrow & \mathrm{NH_4^+} & + \mathrm{Cl^-} \\ 0.004 & & 0.004 & 0.004 \end{array}$$

 NH_4^+ is the conjugate acid of the weak base NH_3 and \therefore is a weak acid.

$$\therefore \text{ K}_{\text{A}} = 5.62 \text{ x } 10^{-10} = \frac{x^2}{0.004 - x}$$

$$0.004 \implies 100 \ge 5.62 \ge 10^{-10}$$

$$\therefore 5.62 \ge 10^{-10} = \frac{x^2}{0.004}$$

$$\therefore x = [H^+] = \sqrt{[HA]}K_A = \sqrt{0.004 \ge 5.62 \ge 10^{-10}}$$

$$\therefore \qquad x = [H_3O^+] = 1.50 \ge 10^{-6}$$

$$\therefore$$
 pH = $-\log_{10}[1.50 \times 10^{-6}]$ = **5.82**

(f) Diethylamine (similar to ammonia) is a weak base (B)

$$K_B = \frac{K_W}{K_A \{ (C_2 H_5)_2 NH \}} = \frac{x^2}{0.033 - x}$$

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$$pK_A = -log_{10}K_A = 10.98$$

 \therefore K_A = 1.05 x 10⁻¹¹ (taking inverse log₁₀ of both sides)

$$\therefore K_{\rm B} = \frac{1.0 \,\mathrm{x} \,10^{-14}}{1.05 \,\mathrm{x} \,10^{-11}} = 9.5 \,\mathrm{x} \,10^{-4} = \frac{x^2}{0.033 - x}$$

$$0.033 >>/100 \times 9.5 \times 10^{-4}$$
 \therefore cannot approximate

We must solve the quadratic

$$\therefore \qquad x^2 + 9.5 \times 10^{-4}x - (9.5 \times 10^{-4} \times 0.033) = 0$$

where
$$a = 1, b = 9.5 \times 10^{-4}, c = -(0.033 \times 9.5 \times 10^{-4})$$

$$x = \frac{-9.5 \times 10^{-4} \pm (90.25 \times 10^{-8} + 4 \times 0.033 \times 9.5 \times 10^{-4})^{\frac{1}{2}}}{2}$$

Hence x =
$$0.51 \times 10^{-2} = [OH^{-}]$$

 $\therefore pOH = -\log_{10} \times .0051 = 2.29$
 $\therefore pH = 14.00 - 2.29 = 11.71$

(g)

 $\mathrm{CN}^{\-}$ is the conjugate base of the weak acid HCN \therefore the solution is basic

$$\therefore CN^{-} + H_2O \qquad \leftrightarrows \qquad HCN + OH^{-}$$

$$0.137 - x \qquad \qquad x \qquad x$$

$$K_B = \frac{K_w}{K_A} = \frac{10^{-14}}{4.8 \,\mathrm{x} \, 10^{-10}} = \frac{x^2}{0.137 - x}$$

$$K_B = 2.1 \times 10^{-5} = \frac{x^2}{0.137 - x}$$

 $0.137 >> 100 \ge 2.1 \ge 10^{-5}$: can approximate.

$$\therefore \qquad x^2 = 0.137 \text{ x } 2.1 \text{ x } 10^{-5} = 2.9 \text{ x } 10^{-6}$$
$$\therefore \quad x = [\text{OH}^-] = 1.7 \text{ x } 10^{-3}$$
$$\therefore \text{ pOH} = 2.77$$

 $\therefore \text{ pH} = 14 - 2.77 = 11.23$

3. (a)

(i) A Brönsted-Lowry acid is a substance which donates a proton (H⁺) to a more basic substance.

e.g. hydrogen chloride or acetic acid dissolved in water.

 $\begin{array}{rcl} HCl + H_2O & \longrightarrow & H_3O^+ + Cl^- \\ CH_3COOH + H_2O & \leftrightarrows & H_3O+ + CH_3COO^- \end{array}$

(ii) A buffer solution is one which resists pH changes. It retains a constant pH despite the addition of relatively small amounts of acid or base.

e.g. a solution containing a weak acid and a salt of the weak acid with a strong base $(HA + Na^{+}A^{-})$

OR

A solution containing a weak base and a salt of the weak base with a strong acid $(B + BH^+A^-)$.

(b)

(i) <u>Buffer capacity</u> is the ability of a buffer to resist pH changes caused by the addition of extra acid or base to the buffer solution. It is determined by the concentrations of the acid and conjugate base. High concentrations of both species give a high buffer capacity when the through the buffer ratio = [Base]/[Acid] is around 1.

(ii) <u>Indicator working range</u> is the 2 pH unit range where the acid/base indicator changes colour from the acid to the base form in response to pH changes in solution.

The range is centered on $pH = pK_{In} + 1$ and should fall in the equivalence point region of a pH titration.

4. (a)

(i)
$$HA + H_20$$

 $0.1 - x$
 x
 $H_3^+O + A^ (A^- = propionate)$
 $K_A = 1.26 \times 10^{-5} = \frac{x^2}{0.1 - x}$
 $0.1 >> 100 \times 1.26 \times 10^{-5}$ we can approximate
 $\therefore x = \sqrt{0.1 \times 1.26} \times 10^{-5} = 1.12 \times 10^{-3}$
 $x = [H_3O^+] = 1.12 \times 10^{-3}$
 $\therefore pH = -log_{10}[1.12 \times 10^{-3}] = 2.95$



Phenol red would be the most suitable indicator, because it changes colour over pH range ~7-9 which coincides with the equivalence point.