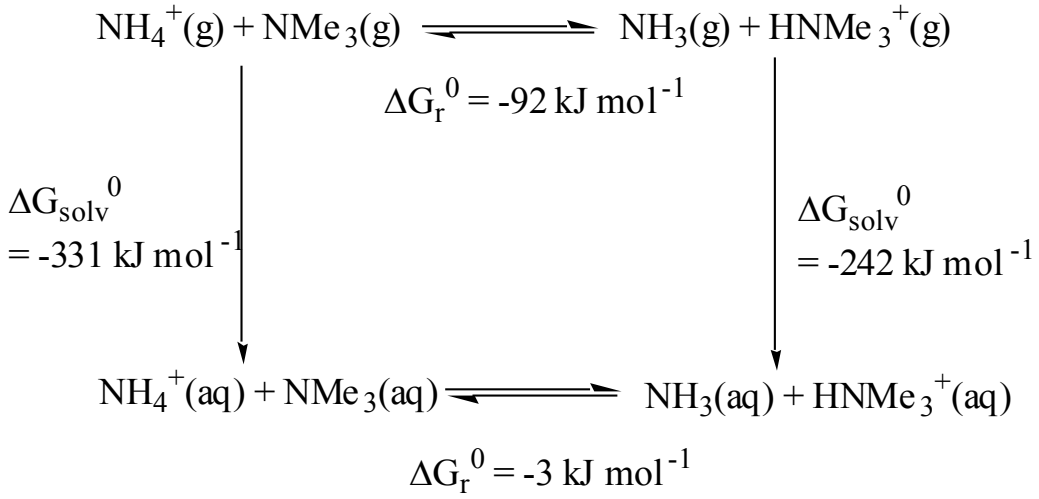
3.I8 - Solvents and Solvent Effects

a) i)

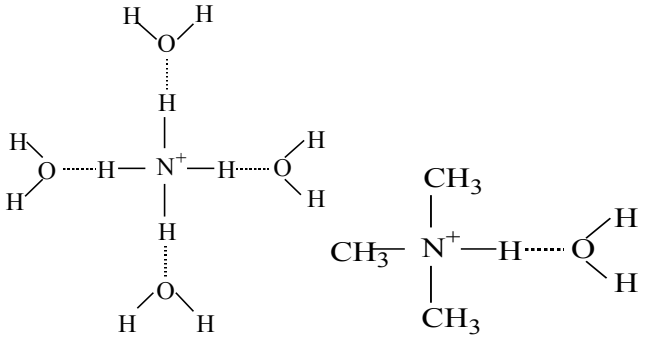


(**1 mark each for labelling ΔG_{rxn} for the gas phase, ΔG_{rxn} in water, ΔG_{solv} in the gas phase and ΔG_{solv} in water – numerical values are unnecessary**)

ii) ΔG_{rxn} = -3 + (-331 + 242) = -92 kJ/mol. (**1 mark for value, 1 mark for units**)

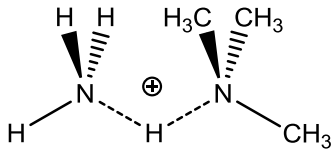
iii) $N(CH_3)_3$ is the stronger base in the gas phase (**1 mark**) because the ΔG_{rxn} is negative (**1 mark**). Also acceptable is a legitimate chemical reason, such as alkyl groups donating electron density into the nitrogen's lone pair or the increased size giving increased polarizability.

iv) There is very little difference in the solvation of the neutral molecules (**1 mark**) since the lone pair is accessible. However, the alkyl groups prevent solvation of the ammonium centre in the charged molecules (**1 mark**), reducing hydration and therefore lowering the stability of the tetramethylammonium centre.



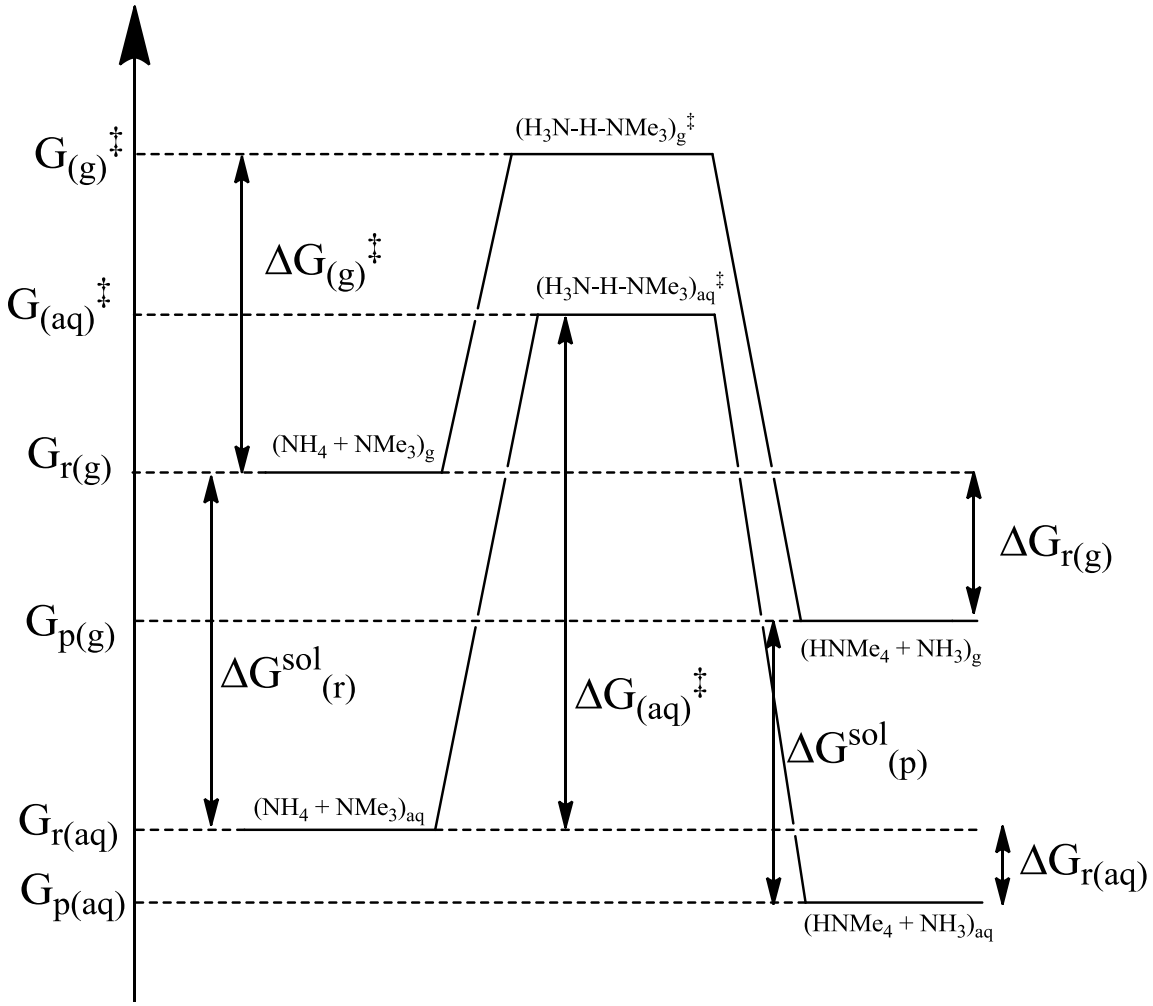
(Drawings optional)

v)



(**0.5 marks each for the shared proton, the partial bonds, the delocalized charge and the stereochemistry**)

vi)

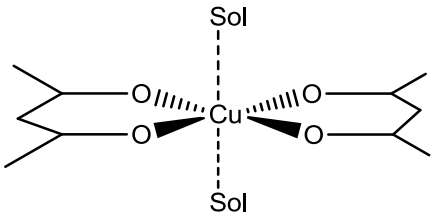


(**0.5 marks for having each state in approximately the correct location according to the known sizes of the ΔG's, 0.5 marks for labelling each ΔG**)

vii) The solvent effect on the rate of reaction will be setermined by the relative solvation of the reactants and the transition state. (**0.5 marks each**)

b) i) A solvatochromic scale could be developed by using ν_{max} as an energy parameter. (**1 mark**)

ii)



(**1 mark for square planar Cu(acac)$_2$, 1 mark for octahedral solvated complex**)

The solvent molecules complex to the copper metal centre (**1 mark**) through electron pair donation (Lewis base) (**1 mark**).

iii) The energy of transition will be lower in more polar solvents because the solvent donates electron density to the metal centre (**0.5 marks**) thus lowering the energy gap between the ground state and the excited state (**0.5 marks**).

c)

i) An LSER will require an energy term (ln (k_2) and a parameter (the Kirkwood parameter). Calculating these:

Solvent	**ε**	$\frac{\varepsilon - 1}{2\varepsilon + 1}$	**k_2 (s^{-1} M^{-1})**	**ln (k_2)**
Toluene	2.3	0.232	$1.0*10^{-4}$	-9.21
Dichloromethane	8.4	0.416	$1.0*10^{-2}$	-4.61
Acetone	21.5	0.466	$3.5*10^{-2}$	-3.35
Nitrobenzene	37.3	0.480	$5.0*10^{-2}$	-3.00

Fitting a line to the first and fourth points (any 2 will suffice):

Slope = (-3.00+9.21)/(0.480-0.232) = 25
Intercept = (-3.00) – (25)*(0.480) = -15

So the LSER would be:

$$\ln(k_2) = 25 * \frac{\varepsilon - 1}{2\varepsilon + 1} - 15$$

(**1 mark for slope, 1 mark for intercept, 1 mark for using ln k_2**)

ii) ε = 5.4, so $\frac{\varepsilon - 1}{2\varepsilon + 1} = 0.373$

Plugging this in to the LSER yields:

$\ln(k_2) = (25) * (0.373) - 15 = -5.675$
$k_2 = \exp(-5.675) = 3.4*10^{-3}\ s^{-1}\ M^{-1}$

(**0.5 marks for value, 0.5 marks for units**)

iii) The rate in methanol from the LSER:

iv) $\varepsilon = 32$, so $\frac{\varepsilon - 1}{2\varepsilon + 1} = 0.477$

$\ln(k_2) = (25) * (0.477) - 15 = -3.08$
$k_2 = \exp(-3.08) = 4.6*10^{-2}\ s^{-1}\ M^{-1}$

Which is much larger than the experimental value. (**1 mark**)

Methanol is a hydrogen bond donating solvent, and none of the ones used in the LSER were, so hydrogen bonding must be causing the problem. (**0.5 marks**)

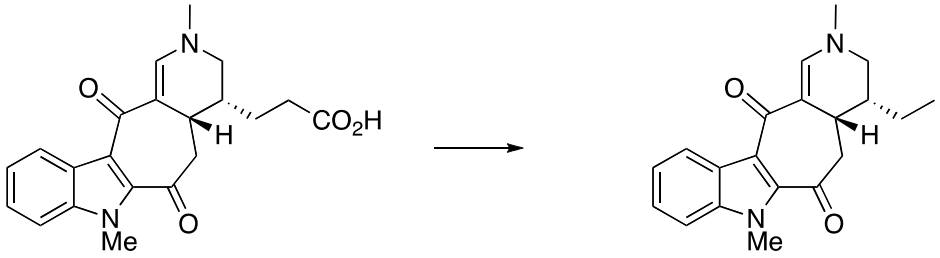
Methanol can hydrogen bond to the amine, thus lowering the energy of the reactants relative to the transition state, which will increase $\Delta G^{\ddagger}$ and slow the reaction down. (**0.5 marks**)

3. O5 REACTIVE INTERMEDIATES

Answer **ALL** parts, (a)-(c)

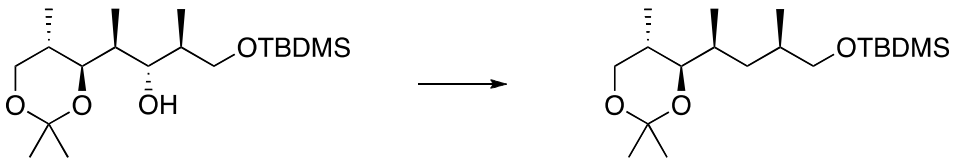
(a) Suggest a radical-based method for carrying out **ONE** of the following transformations, giving reagents and a mechanism. More than one step may be required.

(i)



Barton decarboxylation

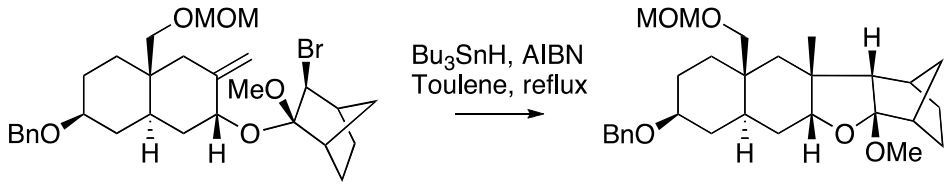
(ii)



Barton-McCombie deoxygenation

(5 marks)

(b) Provide a mechanism for the following transformation commenting on any aspects of selectivity.



Chain mechanism propagated by tributyltin radical and initiated by homolysis of AIBN (i) Dehalogenation by tributyltin radical to give carbon centred radical (ii) intramolecular 5-exo-trig ring-closure to give cis fused 5-5 system (iii) capture of new radical by tributyltinhydride.

(5 marks)

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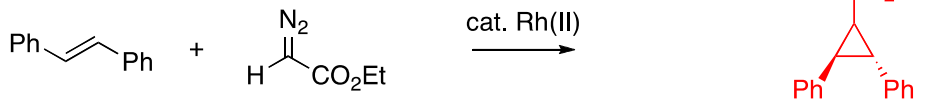
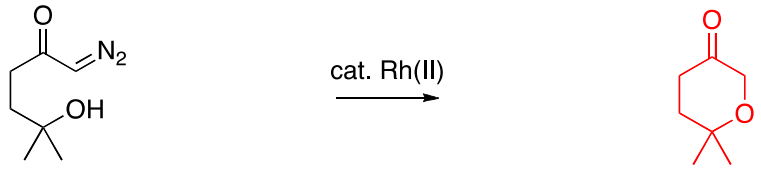
(c) Give the products and mechanisms for **THREE** of the following reactions, noting carefully important regiochemical or stereochemical aspects.

(i)



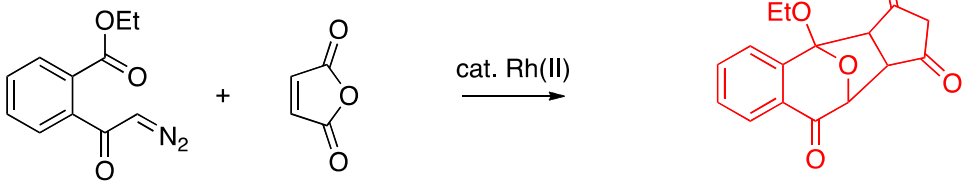
Cyclopropanation via
singlet rhodium carbenoid

(ii)



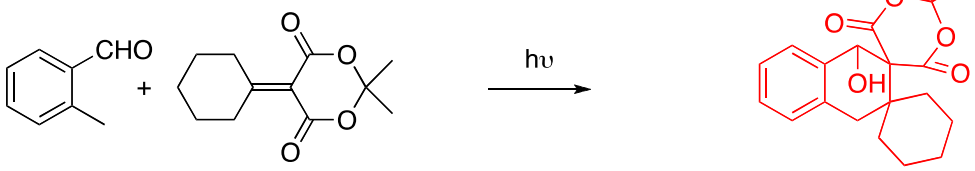
Heterocycle formation via singlet
rhodium carbenoid and insertion
into OH bond

(iii)



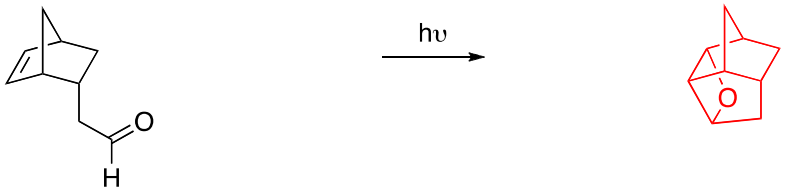
1,3-dipole fomation via singlet
rhodium carbenoid and subsequent [3+2]
cycloaddition

(iv)



Photoenolisation and [4+2]
cycloaddition with rearomatisation

(v)



intramolecular Paterno-Büchi rxn
with photoexcited aldehyde

(5 marks each)

O10. ORGANIC MOLECULAR MODELLING. 2010-2011 Outline Answers.

a)

i) A reasonable discussion on these principle aspects is expected (but not a comprehensive one): Molecular Mechanics or Quantum mechanics provides a total energy which is expanded as a Taylor theorem to provide an estimate for Δx (the correction to any coordinate) from the relationship $\Delta x = -G.H^{-1}$. The technique of geometry optimisation uses this algorithm to minimise the energy for all 3N-6 degrees of freedom, using one of three approximate and one exact way of specifying the H matrix.

ii) Mechanics should not be used, since the parameters for a sp2 carbon (carbene) and those for sp2 carbon (double bond) cannot be compared. Also, mechanics cannot be used to break or form bonds. Quantum mechanics is the only method that can be used, and this can provide a free energy for the reaction, and via a reaction coordinate calculation, a free energy of activation for the reaction.

iii) Visualisation: Con, no coordinates available since it has never been made. Molecular mechanics: Pro; lots of close H…H contacts expected, which are well handled via the non-bonded (van der Waals) terms. Con; the C=C is likely to be much longer than normal. Mechanics is parameterised on normal bond lengths, and the assumption of a quadratic potential for the stretching of a bond, so the longer the bond, and the less accurate its prediction. Also cross terms (e.g. stretch-bend) are not included in most implementations, such as MM2 (i.e. a long length may impact the angles at the affected carbon). DFT: Pros; Good at forming/breaking bonds, good at dealing with unusual bond types, good at computing the entropic contributions.

b)

i) Mechanics would give a good analysis of the dispersion interactions between the two monomers, and a less good analysis of the unusual hydrogen bonding present. It would not routinely enable the entropy of dimerization to be calculated. DFT methods would need to include a dispersion-correction to compete with mechanics, but can be made to include the entropic contribution.

ii) Visualisation (X-ray structure) shows the hydrogen bonding involving the OH group to be unusually to a π-face, which precludes mechanics (unlikely to be parameterised for this kind of H-bond). DFT can provide information about the electronic distribution in the region of the H-bond. Evaluating that distribution by inspecting the molecular orbitals does not allow the inductive effect of the CF3 group to be properly modelled. An electrostatic potential for the monomer reveals the location of the OH…π interaction nicely. Another suitable method is quantum topology, involving calculating the dimer, and locating intermolecular (bond) critical points (BCPs) in the electronic distribution.

iii) Visualisation can provide distances between X or Y and close atoms; the strengths could be very approximately estimated from comparing these distances with the sum of the van der Waals radii of those atoms. Anther method would be the quantum topological method which can be used to identify any intramolecular bond critical points (BCP) in the electron density distribution of the dimer, found from X or Y to any other atoms they are not already covalently bonded to. The value of the electron density at the BCP is approximately linearly related to the strength of the interaction.

c)

i) This is a reaction, involving both forming and breaking bonds. So a density function (DFT or semi-empirical) method is appropriate. A rate constant is obtained from the free energy of activation for the reaction, so a transition state for the process must be located. This is done by the process of geometry minimisation, but using an algorithm that ensures the 2^{nd} derivative (Hessian) matrix has exactly one negative root (eigenvalue) and that the resulting (eigen)vectors (displacement coordinates) correspond to the desired reaction. The transition state can have both twist-boat and chair conformations which both have to be located.

ii) The factors are predominantly steric interactions (or attractions) between the two methyl groups and X=Me. The transition state for the reaction in either a chair or boat conformation has to be modelled with a method capable of breaking/forming bonds (DFT or semi-empirical), and ideally of handling any van der Waals interactions (by including a dispersion correction) and the free energy of that transition state is compared for the two diastereomeric forms to establish their relative concentrations.

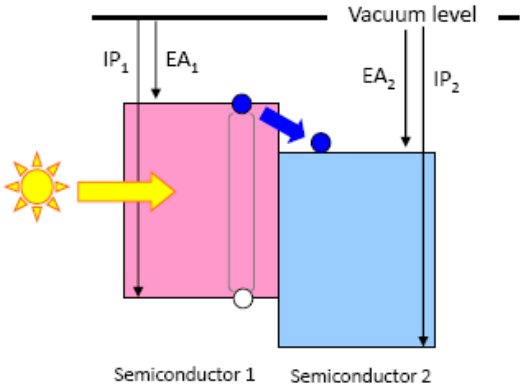
iii) X has to be chiral (a chiral auxiliary. The same procedure as in the previous part is followed, but now all four (in equivalent because of chiral X) transition states have to be located and their relative free energies compared.

3.P6 - Molecular Electronic Materials

Answer part a) **AND EITHER** part b) **OR** part c)

a) Answer **ALL** parts of this question.

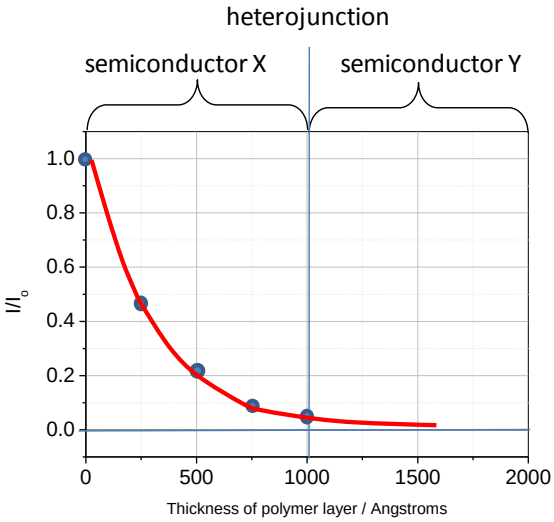
i) Answer should include discussion of Frenkel excitons. High binding energy of excitons in organic semiconductors means that at room temperature very few free electrons and holes. To overcome this problem use an interface or electron donor-acceptor interface to overcome columbic attraction of electrons and holes. Draw labelled diagram of donor-acceptor interface (3 marks)



Excite semiconductor 1:
Electron transfer

ii) 3 marks: Absorption profile should follow: $I = I_o \exp(-kx)$

With k = 0.003 / angstrom then absorption profile should look like



iii) Define n as Ndis/Ncreated then:

$$\frac{N_{dis}}{N_{created}} = \frac{\int_{x_i-L}^{x_i+L} I_o \exp(-kx)\,dx}{\int_0^{\infty} I_o \exp(-kx)\,dx}$$

$$\frac{N_{dis}}{N_{created}} = \frac{\left[-\frac{I_o}{k}\exp(-kx)\right]_{x_i-L}^{x_i+L}}{\left[-\frac{I_o}{k}\exp(-kx)\right]_0^{\infty}}$$

$$\frac{N_{dis}}{N_{created}} = \frac{\exp(-kx_i - kL) - \exp(-kx_i + kL)}{-1}$$

$$\frac{N_{dis}}{N_{created}} = \frac{\exp(-kx_i)\,[\exp(-kL) - \exp(+kL)]}{-1}$$

Assumption: kL << 1
Therefore: exp(+kL) approximately = 1 + kL
exp(-kL) approximately = 1 - kL

$$\frac{N_{dis}}{N_{created}} = \frac{\exp(-kx_i)\,[1 - \mathrm{kL} - 1 - \mathrm{kL}]}{-1}$$

$$\boxed{\frac{N_{dis}}{N_{created}} = 2kL\ exp(-kx_i)}$$

(5 marks)

iv) Using the values of k = 0.003 / Angstrom and L = 60 angstroms, thickness of polymer X = 1000 Angstroms then n = 0.017. This would significantly reduce QE.

Can overcome this problem by using a blend of the two polymers X and Y where the interfaces are structured on exciton diffusion length of 60 Angstroms.

(4 marks)

b) Answer **ALL** parts of this question.

i) 3 marks: Charge transport in an organic semiconductor is a thermally activated hopping process. Each hop assisted by an electric field. In practice carrier transport proceeds via a series of hops between molecules. Such hops are the rate limiting step in transport. In practice the smaller the interchain (inter molecule) distance, the better the charge transport
Each hop / jump can be assisted by an applied field, thus there is a field-dependence to the mobility (termed a Poole-Frenkel type mobility). Mobility can be given by: $\mu = \mu_o \exp\left(\alpha\sqrt{E}\right)$

ii) 2 marks: An organic solar cell: need to high electron and hole mobility in the electron transporting and hole transporting material respectively. High charge carrier mobility needed to minimize charge recombination between the photogenerated electrons and holes. The QE depends on the probability of electrons and holes not recombining.

2 marks: for an OLED need to balanced electron and hole mobility to avoid leakage currents. Easier achieved in multilayered structures as opposed to single layer devices.

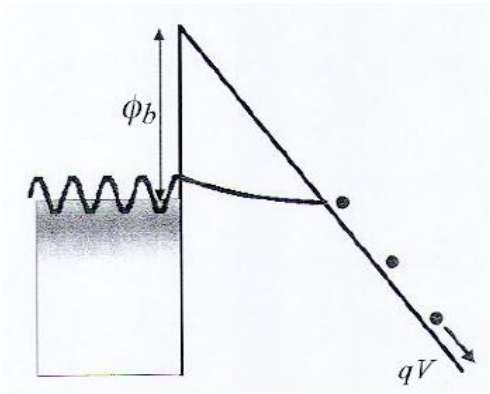
iii) 2 marks: Mobility = 5.36 x 10^{-6} $m^2V^{-1}s^{-1}$

c) Answer **ALL** parts of this question.

i) 2 marks: Fowler Nordheim: A particular case of quantum mechanical tunnelling through a barrier. If there is an injection 'barrier' for electron or hole injection, applying a voltage will cause a field drop across insulator. This creates a barrier across which electrons or holes can tunnel.

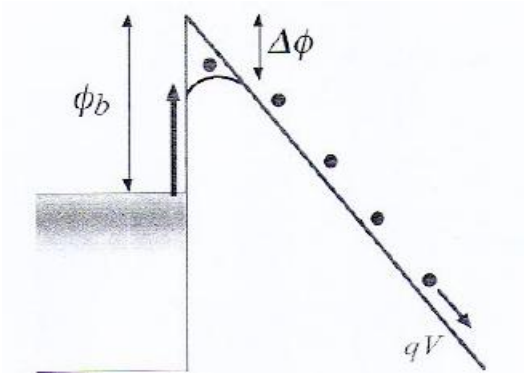
$$J \propto E^2 exp\left(\frac{-B\phi^{3/2}}{E}\right)$$

$k = B\phi^{3/2}$
E = electric field
J is the current
ϕ = barrier height (same as ϕ_b)

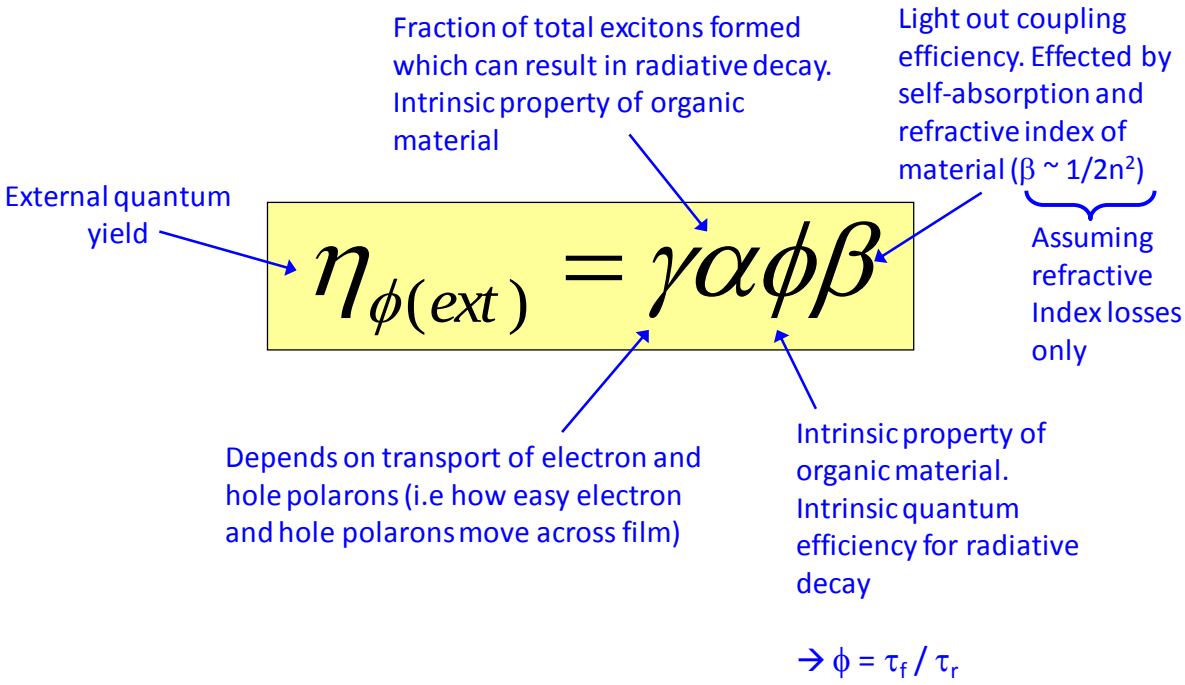


- 2 marks: Thermionic emission: Here, electrons or holes have enough thermal energy to 'hop' over the barrier into the organic semiconductor. However barrier height is actually lowered due to an 'image-force'. The image force results from the attractive Coulombic force that any charge experiences close to a metallic surface. Here, the barrier is lowered by an amount phi(f)

$$J \propto T^2 exp\left(\frac{-[\phi_b - \Delta\phi]}{kT}\right)$$



ii) Answer should include:



Can optimize gamma by chosen multilayered structured to reduce leakage currents. In fluorescent materials alpha = 0.25 (due to singlet/triplet ratio). Can optimize alpha by using triplet emitters – can use compounds with heavy metals. Can optimize phi by using materials with high QE of luminescence.
Light out coupling can be improved by controlling refractive index of material.

3.P10 - Soft Condensed Matter

Answer part (a) and **EITHER** part (b) **OR** part (c).

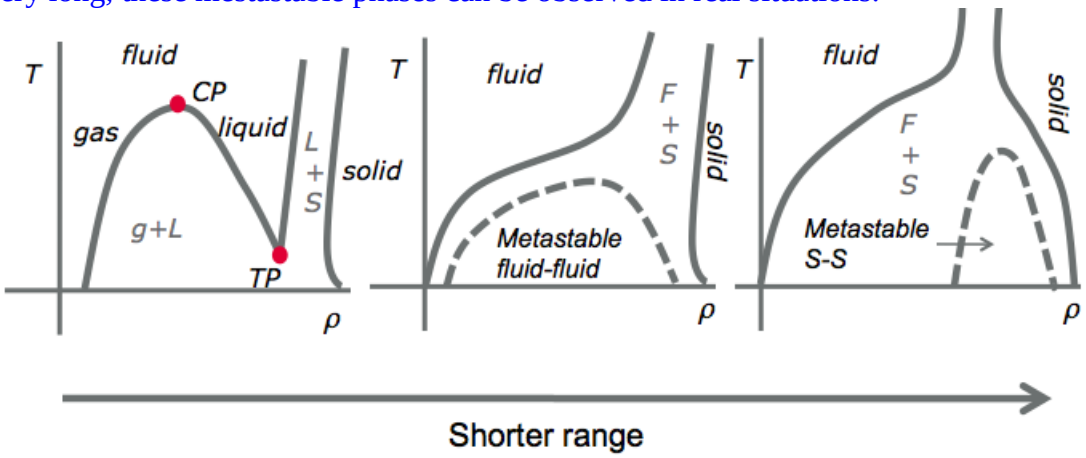
a) Answer **ALL** parts of this question

i) With the aid of suitable graphs briefly discuss how the range of the interactions influences the coexistence diagram of soft materials.

(3 marks)

ANSWER

When the range is long enough, we have got a stable liquid phase, for short-range interactions the liquid phase is not stable and metastable fluid-fluid and solid-solid phases might appear. The mestastable phases appear because the relaxation to the thermodynamic stable phases is very long, these mestastable phases can be observed in real situations.



Diagrams (2 marks), explanation (1 mark).

(3 marks)

ii) The Bjerrum length is an estimate of the interaction range between two charged colloids in a suspension. In an experiment, it is observed that the colloid liquid phase becomes unstable when the interaction range is about 20 nm. Estimate the dielectric constant of the suspension.

Data [Colloids charge = 5 e, T = 300 K]

ANSWER

The Bjerrum length is defined by, $$l_B = \frac{q_i q_j e^2}{4\pi\varepsilon\varepsilon_o k_B T}$$

If the liquid phase becomes unstable at 2 nm, this means that the interaction is of the order of kT at that distance. Hence, substituting in the Bjerrum length equation we get

$$l_B = \frac{q_i q_j e^2}{4\pi\varepsilon\varepsilon_0 k_B T} \Rightarrow$$

$$\varepsilon = \frac{20^2 e^2}{l_B 4\pi\varepsilon_0 k_B T} = \frac{5^2 e^2 (C^2)}{2\times10^{-8}(m)4\pi(8.854\times10^{-12}J^{-1}C^2m^{-1})k_B(J/K)300(K)} = 69.6$$

(3.5 marks)

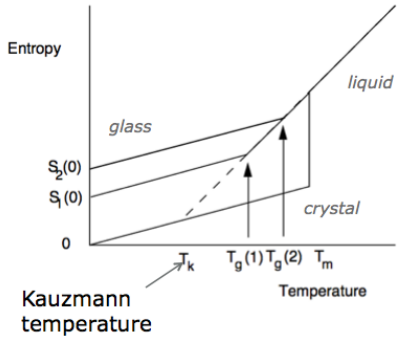
Correct equation for Bjerrum length (1 mark), method/justification (1 mark), correct result (1.5 mark)

iii) For a glass, sketch the dependence of the entropy with temperature, indicating the location of the Kauzmann temperature. Briefly explain the physical meaning of this temperature.

How does the speed of undercooling affect the entropy dependence with temperature? Justify your answer.

(3.5 marks)

ANSWER
The diagram should look like.



The Kauzmann temperature corresponds to the intersect of the entropy of the supercooled liquid with the entropy curve of the crystalline solid. Because the entropy of the glass cannot be smaller than that of the crystal the Kauzmann T marks a lower limit in the experimental glass transition temperature.

The slower the liquid is cooled the longer the time available for configurational sampling and hence the colder the liquid can become before falling in the glass state. Hence the glass transition temperature decreases with the speed of undercooling.

Diagram (1.5 marks), Kauzmann temperature (1 mark), dependence of S with undercooling (1 mark).

(3.5 marks)

iv) The relaxation time for configuration rearrangements in a glass is given by the Vogel-Fulcher equation,

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right)$$

The glass transition temperature of an experiment performed in a 10^4 seconds timescale is 200 K. Estimate the glass transition temperature when the experimental time increases by two orders of magnitude, 10^6 seconds.

Comment on your result.

[Data: B = 10^3 K, T_0=50 K]

(5 marks)

ANSWER

We identify the experimental time with τ. Hence,

$$\ln \tau_1 = \ln \tau_0 \frac{B}{T_1 - T_0}$$

$$\ln \tau_2 = \ln \tau_0 + \frac{B}{T_2 - T_0}$$

$$\ln \frac{\tau_2}{\tau_1} = \frac{B}{T_2 - T_0} - \frac{B}{T_1 - T_0}$$

which simplifies to:

$$\frac{1}{B} \ln \frac{\tau_2}{\tau_1} + \frac{1}{T_1 - T_0} = \frac{1}{T_2 - T_0}$$ hence we get, T2 = 138.7 K

The glass transition temperature decreases; this is consistent with a slower cooling rate in the experiment, i.e., with a longer experimental time. This gives more time to the molecules to relax towards the equilibrium positions (the equilibrium positions are not reached in the experimental time).

Correct identification of tau with experimental time (1 mark) , correct derivation of equation and result (3 marks), justification (1 mark).

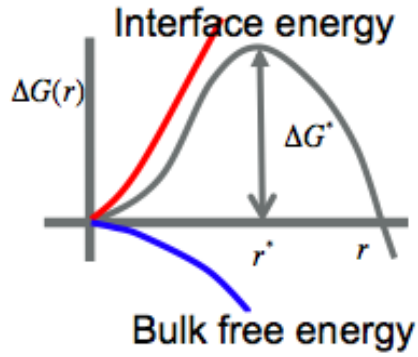
b) Answer **ALL** parts of this question

i) For a homogeneous nucleation process, sketch the dependence of the Gibbs free energy with the radius of a spherical nucleus. Justify your answer by discussing the different contributions to the Gibbs free energy.

(3 marks)

ANSWER

The Gibbs free changes as



Two terms contribute to this. A volume term (blue line), ~r^3, which takes into account the gain in free energy associated to the formation of the crystal, and a surface term that is connected to the work required to create the crystal-liquid interface (red line), ~r^2. The balance of these contribution results in a maximum, this is the activation free energy for the formation of the critical nucleus of radius r*.

Correct sketch (1.5 marks), explanation, (1.5 marks). Total 3 marks

ii) Show that the radius of the critical nucleus for homogeneous nucleation is given by the following equation:

$$r^* = \frac{2\gamma_{sl} T_m}{\Delta H_m \Delta T}$$

Define all the terms in this equation.

(7 marks)

ANSWER

-gamma_sl is the solid-liquid surface tension
-Tm is the melting temperature
-Delta H_m: is the enthalpy of melting
-Delta T: is the undercooling, = Tm – T, T is the temperature of homogeneous nucleation.

Derivation.

Start with the definition of the Gibbs free energy

$$\Delta G(r) = \Delta G_b 4/3\pi r^3 + \gamma_{sl} 4\pi r^2$$

The critical nucleus is defined by the radius that maximizes the free energy, i.e.,

$\left(\frac{\partial G}{\partial r}\right)_{r=r^*} = 0$, hence $r^* = \frac{2\gamma_{sl} T_m}{\Delta H_m \Delta T}$

$\Delta G_b 4\pi r^2 + \gamma_{sl} 8\pi r = 0 \Rightarrow r[\Delta G_b 4\pi r + \gamma_{sl} 8\pi] = 0$

Rearranging we get, $r^* = \frac{-2\gamma_{sl}}{\Delta G_b}$ (1)

Now we recall the definition of entropy in terms of the Gibbs free energy.

$\Delta S_m = \left(\frac{-\partial G_l}{\partial T}\right)_P - \left(\frac{-\partial G_s}{\partial T}\right)_P = \frac{\Delta H_m}{T_m}$ at equilibrium

Considering, $-S = (\partial G/\partial T)_P$ and that the derivative is constant for the undercooling range $\Delta T = T_m - T$, we get the new equation.

$\Delta G_b = \frac{-\Delta H_m}{T_m}\Delta T$ and substituting in (1)

$r^* = \frac{2\gamma_{sl}}{\Delta H_m}\frac{T_m}{\Delta T}$ as requested.

Correct definitions (1 mark), equation for the free energy (1 mark), stationary condition and critical radius --equation 1 above-- (2 marks) connection between Delta G_b and Delta H_m and final result (3 marks).

c) Answer **ALL** parts of this question

i) A colloidal suspension coagulates when the average distance between the colloids is 1 nm. Estimate the *molar* concentration of KCl needed to destabilize the suspension at 300 K.

[Data: water dielectric constant: 78]

(5 marks)

ANSWER

According to the DLVO theory the coagulation will occur when $\kappa_D h_0 \sim 1$ where kappa_D is the Debye length and h_0 is the separation between the colloids. Hence

$\kappa_D = \left(\frac{e^2 \sum_{i=1} \rho_i z_i^2}{\varepsilon \varepsilon_0 k_B T}\right)^{1/2}$ using the condition from the DLVO theory:

$$\frac{(\kappa_D h_0)^2 \varepsilon\varepsilon_0 k_B T}{2e^2 z^2} = \rho_{KCl} h_0^{\ 2} = \frac{1\times 78\times 8.854\times 10^{-12}(J^{-1}C^2 m^{-1})\times k_B(JK^{-1})\times 300(K)}{2\times(1.602\times 10^{-19})^2(C^2)\times 1}$$

$$\rho_{KCl} = 5.5\times 10^7 / h_0^2 = 5.5\times 10^{25}$$

ion pairs/m^3. In mols 0.09 M.

(1 mark) recognize kappa_d h_0 ~ 1, (1 mark) state Debye length equation, (3 marks) correct calculation of the concentration in right units M.

ii) Experimental studies have shown that the van der Waals interactions between colloidal particles dispersed in a solvent can be repulsive, attractive or zero depending on the suspension composition.

Explain these observations. You answer should contain a reference to the relevant equations.

(5 marks)

ANSWER

The van der Waals interactions between colloidal particles can be written as:

$$U_{vdw}(h) = \frac{-A}{6h}\frac{(R_1 R_2)}{(R_1+R_2)}$$

Where h is the surface to surface distance, and R1 and R2 the radii of the colloids. A is the Hamaker constant which depends on the medium and colloid compositions through $A \propto (\rho_{c1}\alpha_{c1} - \rho_s\alpha_s)(\rho_{c2}\alpha_{c2} - \rho_s\alpha_s)$
Where rho_ci and alpha_ci are the density and polarizability of the colloids and rho_s and alpha_s the density and polarizability of the solvent. Hence for colloids of different composition if one of the terms in the brackets is positive and the other is negative A<0 and the van der Waals interaction would be repulsive. For colloids of the same composition, A>0 attractive as $A \propto (\rho_c\alpha_c - \rho_s\alpha_s)^2$ or "zero" when $\rho_c\alpha_c = \rho_s\alpha_s$. The latter situation can be achieved by using "refractive index matching",as shown by the Clausius Mosotti equation.

$$\frac{n^2-1}{n^2+2} = 4\pi\rho\alpha/3$$

(2 marks),van der waals equation in terms of Hamaker constant and Hamaker constant equation in terms of alpha and rho (2 marks) explanation repulsive/attractive interactions (1 mark) explanation zero interactions (clausius mosotti equations).