

2013 1A Revision

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$$\left(\frac{\partial \mu}{\partial p} \right)_T = V_m$$

$$\int_{\mu^\circ}^{\mu'} \partial \mu = \int_{p^\circ}^{p'} V_m \partial p \quad pV_m = RT$$

$$\int_{\mu^\circ}^{\mu'} \partial \mu = \int_{p^\circ}^{p'} \frac{RT}{p} \partial p$$

$$\mu(g) = \mu^\circ(g) + RT \ln \left(\frac{p}{p^\circ} \right)$$

2012 Liquids & Solutions

Q2 was answered by a significant number of candidates (65%). In general this question was straightforward and well answered. The most common errors arose from inconsistencies in the derivation of Raoult's law, where the chemical potential of the pure component was not considered. Candidates also struggled with a clear explanation of the molecular interactions that give rise to Raoult's and Henry's laws.

Let's consider the vapour-liquid equilibrium...

$$\mu_i(g) = \mu_i(l)$$

For the liquid:

$$\mu_i(l) = \mu_i^*(l) + RT \ln x_i$$

& we just worked out the result for the gas...

$$\mu_i(g) = \mu_i^\circ(g) + RT \ln \left(\frac{p}{p^\circ} \right)$$

So,

$$\mu_i^\circ(g) + RT \ln \left(\frac{p}{p^\circ} \right) = \mu_i^*(l) + RT \ln x_i$$

Now, what is $\mu_i^*(l)$, the chemical potential of pure solvent?

For pure liquid solvent

$$\mu_i^* = \mu_i^\infty(g) + RT \ln \left(\frac{p^*}{p^\infty} \right)$$

So let's substitute...

$$\mu_i^\infty(g) + RT \ln \left(\frac{p_i}{p^\infty} \right) = \mu_i^\infty(g) + RT \ln \left(\frac{p^*}{p^\infty} \right) + RT \ln x_i$$

$$\ln \left(\frac{p_i}{p^\infty} \right) = \ln \left(\frac{p^*}{p^\infty} \right) + \ln x_i$$

$$\ln \left(\frac{p_i}{p^\infty} \right) - \ln \left(\frac{p^*}{p^\infty} \right) = \ln x_i$$

$$\ln \left(\frac{p_i}{p^*} \right) = \ln x_i$$

$$p_i = x_i p^* \quad \dots \text{which is Raoult's law}$$

$$\mu_1(l) = \mu_1^*(l) + RT \ln x_1 + w(1 - x_1)^2$$

- Accounts for the non-zero enthalpy of mixing.
- Results from the non-identical interactions between components.
- The sign of w indicates if non-similar contacts are less favourable ($w > 1$) or more favourable than similar contacts.

$$p_1 = x_1 p_1^* \exp [w(1 - x_1)^2 / RT]$$

As $x_1 \rightarrow 1$

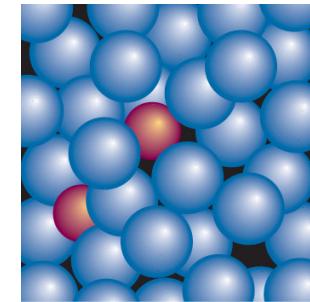
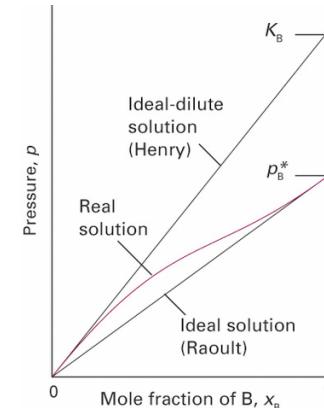
$$p_1 \rightarrow p^* x_1 \quad \dots \text{which is Raoult's law}$$

As $x_1 \rightarrow 0$

$$p_1 \rightarrow x_1 p^* \exp [w / RT]$$

$$p_1 \rightarrow \kappa x_1 \quad \dots \text{which is Henry's law}$$

This describes the transition between all-like contacts (1-1) and all non-like contacts (1-2)



2012 Valence

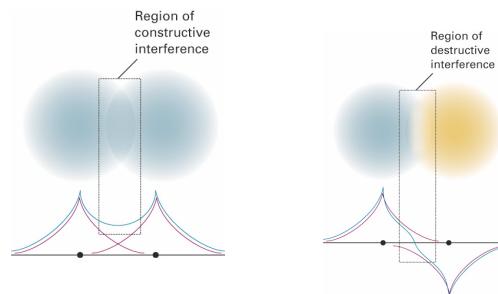
Q5 was a popular choice (82%), presumably due to the descriptive nature of parts of this question. Very few candidates were able to provide an adequate explanation of the differences between valence bond and molecular orbital descriptions of bonding. However, almost no candidates had any trouble with parts (c) and (d).

Discuss...

- Overlap of atomic orbitals (linear combinations):

A wavefunction (molecular orbital) can be written as a linear combination of atomic orbitals localized on specific atoms.

- In-phase and out-of-phase combinations.



- Overlap integrals

Consider the overlap of just two atomic orbitals...

$$\Psi_e = c_A \phi_A + c_B \phi_B$$

As electron density must be equal at all points related by symmetry...

$$|\Psi_e|^2 = c_A^2 \phi_A^2 + c_B^2 \phi_B^2 + 2c_A c_B \phi_a \phi_b \quad c_a = \pm c_B = c$$

We can also normalise the wavefunction, giving rise to overlap integral...

$$c = \left[\frac{1}{2(1 \pm S_{AB})} \right]^{1/2} \quad S_{AB} = \int \phi_A \phi_B dr$$

- Energies

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\Psi^* \Psi d\tau} \quad c = \left[\frac{1}{2(1 \pm S_{AB})} \right]^{1/2}$$

$$E = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}} \quad \Psi_{\pm} = \frac{\phi_A \pm \phi_B}{[2(1 \mp S_{AB})]^{1/2}}$$

- S_{AB} is overlap integral.

- H_{AA} is coulomb integral.

- Sum of orbital energy, attraction of electron on A to B nucleus, plus coulomb repulsion between nuclei.

- (Energy of the electron localized on nucleus A in the presence of nucleus B).

- H_{AB} is resonance integral.

- e.g. attraction of overlap density to nucleus A.

Difference between MO and VB theory?

MO:

Bond formed by electrons occupying molecular orbitals created by the overlap of atomic orbitals.

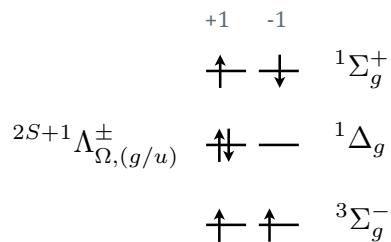
Molecular orbital theory assumes that individual electron pairs are found in molecular orbitals that are distributed over the entire molecule.

VB:

Overlap of partially filled atomic orbitals to form a bond (i.e. each electron belongs to a particular bond).

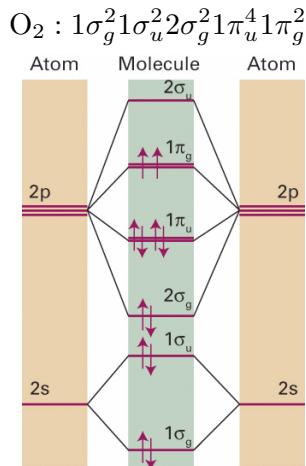
Combine (hybridize) the valence atomic orbitals on a given atom before looking for overlap with orbitals from other atoms.

Term symbols for ground electronic state O₂?



1. The term with maximum multiplicity lies lowest in energy
2. For a given multiplicity, the term with the largest value of L lies lowest in energy.
3. For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.

http://physchem.ox.ac.uk/~hill/static_resources_molecular_term_symbols.pdf

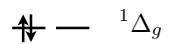
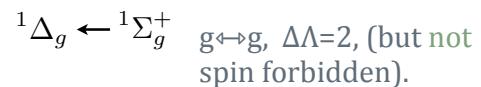
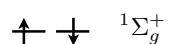


Radiative transitions?

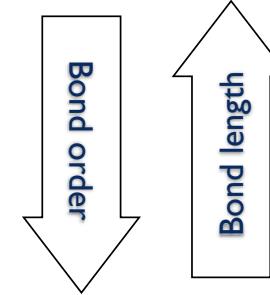
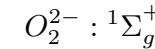
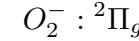
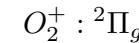
Forbidden by:



- $\Delta\Lambda = 0, \pm 1$
- $\Delta S = 0$, in the absence of spin-orbit coupling
- $\Delta\Omega = 0, \pm 1$
- $\Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^-$
- g↔u



Expect singlet to be long lived. There are no highly-allowed transitions.



2012 Misc

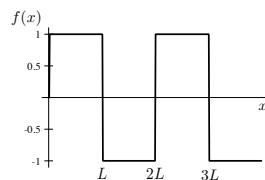
- (a) Very few candidates were able to correctly compute the Fourier transform. (b) Was unpopular.
 (c) Reasonable attempts, although many candidates did not use physical arguments to determine whether a vibrational transition is dipole-allowed. (d) Overall, well answered. (e) Overall, well answered. (f) Although candidates were able to identify the terms in the Butler-Volmer equation, and even correctly apply it, few appeared to have a deeper understanding of the physical chemistry underlying the form of this equation.

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left[a_n \cos\left(\frac{\pi n x}{L}\right) + b_n \sin\left(\frac{\pi n x}{L}\right) \right]$$

$$a_0 = \frac{1}{L} \int_{-L}^L f(x) dx$$

$$a_n = \frac{1}{L} \int_{-L}^L f(x) \cos\left(\frac{\pi n x}{L}\right) dx$$

$$b_n = \frac{1}{L} \int_{-L}^L f(x) \sin\left(\frac{\pi n x}{L}\right) dx.$$



$f(x) = -f(-x)$ This is an odd function.

$$\text{So we can simplify... } a_0 = \frac{1}{L} \int_{-L}^L f(x) dx = 0$$

$$a_n = \frac{1}{L} \int_{-L}^L f(x) \cos\left(\frac{\pi n x}{L}\right) dx = 0$$

$$\text{But no such luck with } b_n = \frac{1}{L} \int_{-L}^L f(x) \sin\left(\frac{\pi n x}{L}\right) dx.$$

$$\begin{aligned} b_n &= \frac{1}{L} \int_{-L}^L f(x) \sin\left(\frac{\pi n x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L f(x) \sin\left(\frac{\pi n x}{L}\right) dx \\ &= \frac{2}{L} \int_0^L \sin\left(\frac{\pi n x}{L}\right) dx \\ &= \frac{2}{L} \left[-\frac{L}{n\pi} \cos\frac{n\pi x}{L} \right]_0^L \\ &= \frac{2}{n\pi} (-\cos n\pi + 1) \end{aligned}$$

so $b_n = 4/n\pi$ if n is odd or zero if n is even. The final Fourier series is thus...

$$f(x) = \frac{4}{\pi} \sum_{n=1,3,5,\dots}^{\infty} \left[\frac{1}{n} \sin\left(\frac{\pi n x}{L}\right) \right]$$

$$\Delta G = \gamma 4\pi r^2 - \frac{4\pi RT}{3v_l} r^3 \ln \frac{p}{p_0}$$

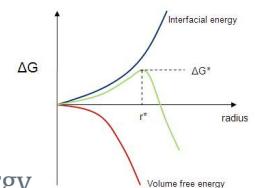
↑
Change in free energy from forming droplet surface.

↑
Change in free energy from the change in vapour pressure due to Laplace pressure relative to the droplet surface.

$$\frac{d\Delta G}{dr} = \gamma 8\pi r - \frac{12\pi RT}{3v_l} r^2 \ln \frac{p}{p_0} = 0$$

$$8\pi\gamma - \frac{12\pi RT}{3v_l} r \ln \frac{p}{p_0} = 0$$

$$r^* = \frac{2v_l\gamma}{RT \ln \frac{p}{p_0}}$$

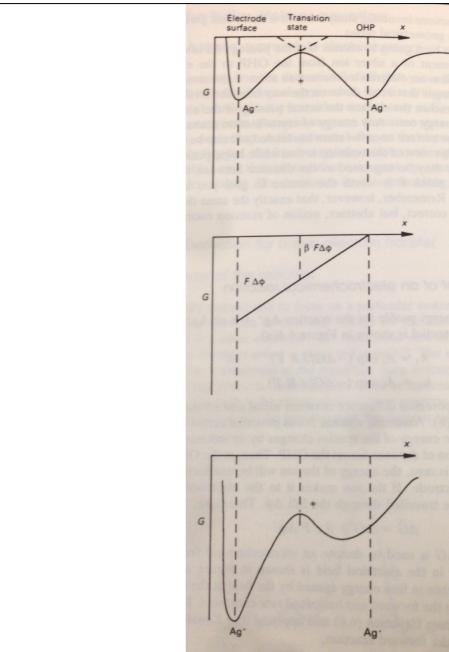


So let's substitute...

$$r^* = \frac{2v_l\gamma}{RT \ln \frac{p}{p_0}}$$

$$\Delta G = \gamma 4\pi r^2 - \frac{4\pi RT}{3v_l} r^3 \ln \frac{p}{p_0}$$

$$\begin{aligned}\Delta G^* &= 4\pi\gamma \left(\frac{2v_l\gamma}{RT \ln \frac{p}{p_0}} \right)^2 - \frac{4\pi RT}{3v_l} \left(\frac{2v_l\gamma}{RT \ln \frac{p}{p_0}} \right)^3 \ln \frac{p}{p_0} \\ &= \left(\frac{2v_l\gamma}{RT \ln \frac{p}{p_0}} \right)^2 \left[4\pi\gamma - \frac{4\pi RT}{3v_l} \left(\frac{2v_l\gamma}{RT \ln \frac{p}{p_0}} \right) \ln \frac{p}{p_0} \right] \\ &= \left(\frac{2v_l\gamma}{RT \ln \frac{p}{p_0}} \right)^2 \left[4\pi\gamma - \frac{8\pi\gamma}{3} \right] \\ &= \frac{16\pi\gamma^3 v_l^2}{3(RT \ln \frac{p}{p_0})^2} = \frac{16\pi\gamma^3}{3} \left[\frac{RT}{v_l} \ln \frac{p}{p_0} \right]^{-2}\end{aligned}$$



$$j = j_0 \left\{ \exp \left(\frac{(1-\alpha)F\eta}{RT} \right) - \exp \left(-\frac{\alpha F\eta}{RT} \right) \right\}$$

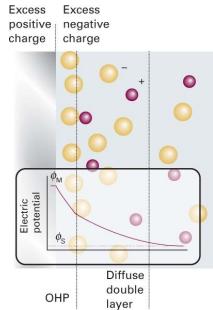


Figure 22.33 A representation of the Stern model of the electrode-solution interface. The model incorporates the idea of an outer Helmholtz plane near the electrode surface and of a diffuse double layer further away from the surface.

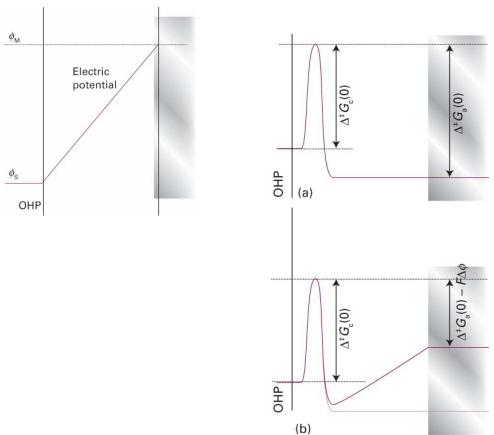


Figure 22.39 When the transition state resembles a species that has undergone oxidation, the activation Gibbs energy for the cathodic current is almost unchanged but the activation Gibbs energy for the anodic current is strongly affected. (a) Zero potential difference; (b) nonzero potential difference.

$$j = j_0 \left\{ \exp \left(\frac{(1-\alpha)F\eta}{RT} \right) - \exp \left(-\frac{\alpha F\eta}{RT} \right) \right\}$$

- j_0 : Exchange current density.
- α : Transfer coefficient.
- η : Overpotential, the difference between anodic and cathodic potentials when current is drawn.

$$\frac{j_2}{j_1} = \frac{j_0 \left\{ \exp \left(\frac{(1-\alpha)F\eta_2}{RT} \right) - \exp \left(-\frac{\alpha F\eta_2}{RT} \right) \right\}}{j_0 \left\{ \exp \left(\frac{(1-\alpha)F\eta_1}{RT} \right) - \exp \left(-\frac{\alpha F\eta_1}{RT} \right) \right\}}$$

Given: 25°C, j_1, η_1, η_2 , and α . So just substitute.

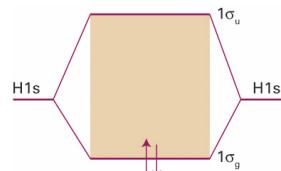
$$j_2 = 8.55 \text{ /mA cm}^{-2}$$

2011 Valence

This was a multipart questions covering relatively familiar ground. Part (a) was the least popular, with very few candidates having much to say about possible improvements to simple MO theory. Part (b) was a little more popular, and most students were able to discuss van der Waals forces. However, only a minority of the School correctly defined the orbital approximation and had something sensible to say about electron correlation. Most candidates attempted parts (c), (d), and (e). Part (e) was very well answered indeed, with many candidates scoring full marks. Part (d) was also well answered, although few candidates could explain why the spin-orbit states of NO(X) were both two-fold degenerate. In part (c), many candidates launched into standard essays on the π^2 configuration and terms that arise, but few could explain why the wavefunction as written was a Σ state. The symmetry properties of the wavefunction were well understood, as too were Fermi holes and Fermi heaps.

MO wavefunctions

$$\begin{aligned}\psi_{1\sigma_g} &= \frac{1}{\sqrt{2}} (\phi_{1s_A} + \phi_{1s_B}) \\ &= \frac{1}{\sqrt{2}} (\phi_A + \phi_B)\end{aligned}$$



Overall spatial wavefunction

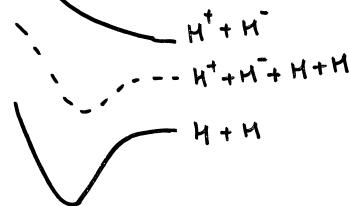
$$\Psi = \psi_{1\sigma_g}(r_1)\psi_{1\sigma_g}(r_2)$$

$$\lim_{r \rightarrow \infty} \rho(r_1, r_2) = |\Psi|^2 \propto \phi_A^2(1)\phi_B^2(2) + \phi_B^2(1)\phi_A^2(2) + \phi_A^2(1)\phi_A^2(2) + \phi_B^2(1)\phi_B^2(2)$$

So in the limit of $r \rightarrow \infty$ there are four non-zero terms corresponding to the dissociation to $H + H + H^+ + H^-$.

$$\lim_{r \rightarrow \infty} \rho(r_1, r_2) = |\Psi|^2 \propto \phi_A^2(1)\phi_B^2(2) + \phi_B^2(1)\phi_A^2(2) +$$

$$\phi_A^2(1)\phi_A^2(2) + \phi_B^2(1)\phi_B^2(2)$$



At very large R , the exact wave function will have one electron near the left proton and one near the right this is the 'covalent' part of the wave function.

The other terms have both electrons near one proton and none near the other, thus creating an ionic wave function. Since the molecular orbital wave function must have equal covalent and ionic contributions, it yields unfavorable energies for large R .

This simple overall wavefunction is missing electron correlation. We need to include a configuration interaction to improve things, mix with higher energy states of the same symmetry.

Muller & Goddard in Encyclopedia of Physical science and Technology 2002

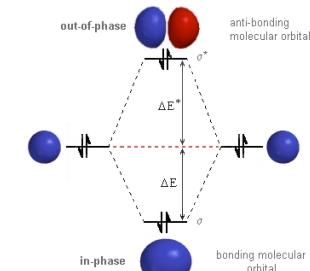
Again, first explain what an MO is. Then...

Simple MO treatment predicts no net bonding for He_2 .

The presence of electrons in the σ^* -anti-bonding orbital prevents He_2 from forming, hence it cancels out the effect of the electrons in the σ -bonding orbital.

Bonding arises from the weak van der Waals interaction, which is associated with the correlated motion of electrons.

This is neglected in simple MO theory as the motions of the electrons is treated as independent.



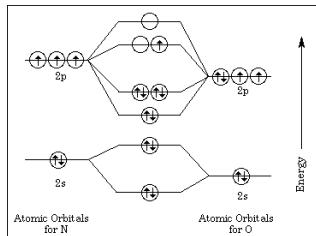
$$\Psi = \frac{1}{2} [\pi_{+1}(1)\pi_{-1}(2) + \pi_{-1}(1)\pi_{+1}(2)] \times (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

Spin wavefunction is associated with a paired spin, hence a singlet state

Spatial wavefunction is associated with $\lambda_1 = +1, \lambda_2 = -1$

So that $|\Lambda| = \lambda_1 + \lambda_2 = 0$ i.e. a Σ state.

So term symbol must be $^1\Sigma$. However a π^2 configuration will also give rise to $^3\Sigma$ and $^1\Delta$ terms. The $^1\Sigma$ is the highest energy because of Fermi heap (application of Hund's rules).

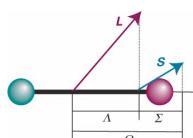


π^1 configuration leads to a $^2\Pi$ term

This is split into $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ spin-orbit states.

Hund's 3rd rule suggests $^2\Pi_{1/2} < ^2\Pi_{3/2}$.

The additional two-fold degeneracy arises from the $\pm\Omega$ components, coupling of electron angular motion to rotational motion (lambda-coupling).



First, state secular equations...

$$\begin{pmatrix} \alpha - \epsilon & \beta & 0 \\ \beta & \alpha - \epsilon & \beta \\ 0 & \beta & \alpha - \epsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

Then solve determinant...

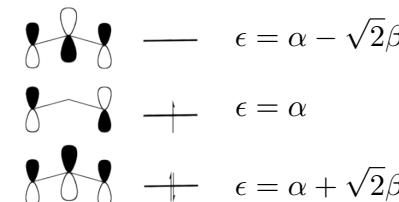
$$\begin{vmatrix} \alpha - \epsilon & \beta & 0 \\ \beta & \alpha - \epsilon & \beta \\ 0 & \beta & \alpha - \epsilon \end{vmatrix} = 0$$

$$(\alpha - \epsilon)^3 - (\alpha - \epsilon)\beta^2 - \beta^2(\alpha - \epsilon) = 0$$

$$(\alpha - \epsilon) [(\alpha - \epsilon)^2 - 2\beta^2] = 0$$

$$(\alpha - \epsilon) [(\alpha - \epsilon) + \sqrt{2}\beta] [(\alpha - \epsilon) - \sqrt{2}\beta] = 0$$

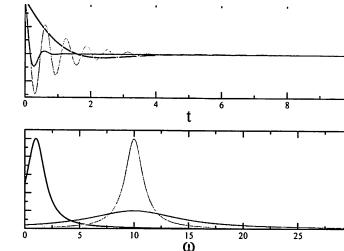
So the solutions are... $\epsilon = \alpha, \alpha \pm \sqrt{2}\beta$



$$\epsilon_{\text{total}} = 3\alpha + 2\sqrt{2}\beta$$

2011 Misc

(a) Very few candidates were able to correctly compute the Fourier transform. (b) Was unpopular. (c) Reasonable attempts, although many candidates did not use physical arguments to determine whether a vibrational transition is dipole-allowed. (d) Overall, well answered. (e) Overall, well answered. (f) Although candidates were able to identify the terms in the Butler-Volmer equation, and even correctly apply it, few appeared to have a deeper understanding of the physical chemistry underlying the form of this equation.



OK, the Fourier Transform is

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\alpha t} \cos \omega_0 t e^{-i\omega t} dt.$$

The function is even in t and so we can write

$$F(\omega) = \frac{2}{\sqrt{2\pi}} \int_0^{\infty} e^{-\alpha t} \cos \omega_0 t \cos \omega t dt.$$

Using addition formulae for $\cos(A \pm B)$ gives

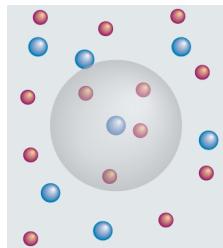
$$\begin{aligned} F(\omega) &= \frac{1}{\sqrt{2\pi}} \int_0^{\infty} \{e^{-\alpha t} \cos(\omega_0 + \omega)t + e^{-\alpha t} \cos(\omega - \omega_0)t\} dt, \\ &= \frac{1}{\sqrt{2\pi}} [I_1 + I_2]. \end{aligned}$$

$\log_{10}\gamma_{\pm}$ is negative because the solution is stabilized by the presence of ions in solution. i.e.

$$\mu_i = \mu_i^\ominus + RT \ln x_i + RT \ln \gamma_i$$

Estimate γ_{\pm} ? Have to remember what solubility product is...

$$K_{sp} = \gamma_{\pm}^2 \left(\frac{m_{\pm}}{m^\ominus} \right)^2$$



Then just convert solubility units ($2.1 \text{ g dm}^{-3} = 1.54 \times 10^{-2} \text{ M}$) and compute. $\gamma_{\pm} = 0.395$

Comment c.f. Debye Hückel? $\log \gamma_{\pm} = -A|z_+ z_-| \sqrt{I}$

$$I = \frac{1}{2} \sum_i \frac{m_i}{m^\ominus} z_i^2 = 4 \times 1.54 \times 10^{-2} = 0.0616 \quad \gamma_{\pm} = 0.31$$

So qualitative agreement, but the solution ionic strength is not really dilute enough for DH theory to be quantitative.

$$\begin{aligned} \text{By parts...} \\ u = \cos At, \quad dv = e^{-\alpha t} dt \\ I_1 &= \int_0^{\infty} e^{-\alpha t} \cos At dt \\ &= \left[\cos At \cdot \frac{-1}{\alpha} e^{-\alpha t} \right]_0^{\infty} - \int_0^{\infty} \frac{-1}{\alpha} e^{-\alpha t} A \sin At dt \\ &= \frac{1}{\alpha} + \frac{A}{\alpha} \int_0^{\infty} e^{-\alpha t} \sin At dt \\ &= \frac{1}{\alpha} + \frac{A}{\alpha} \left\{ \left[\frac{-1}{\alpha} e^{-\alpha t} \sin At \right]_0^{\infty} - \int_0^{\infty} \frac{-1}{\alpha} e^{-\alpha t} \cdot -A \cos At dt \right\} \\ &= \frac{1}{\alpha} - \frac{A^2}{\alpha^2} \int_0^{\infty} e^{-\alpha t} \cos At dt \\ &= \frac{1}{\alpha} - \frac{A^2}{\alpha^2} I_1 \\ I_1 &= \frac{\alpha}{\alpha^2 + A^2}. \end{aligned}$$

By analogy,

$$\begin{aligned} I_2 &= \int_0^{\infty} e^{-\alpha t} \cos Bt dt \\ &= \frac{\alpha}{\alpha^2 + B^2}. \end{aligned}$$

Recalling $A = \omega + \omega_0$ and $B = \omega - \omega_0$ and $F(\omega) = \frac{1}{\sqrt{2\pi}}[I_1 + I_2]$ gives

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \left[\frac{\alpha}{\alpha^2 + (\omega - \omega_0)^2} + \frac{\alpha}{\alpha^2 + (\omega + \omega_0)^2} \right],$$

as required.

Butler-Volmer equation again...Essentially TST applied to the electrode reaction)

$$j = j_a - j_c = Fk_a[\text{Red}] - Fk_c[\text{Ox}]$$

$$j = FB_a[\text{Red}]e^{-\Delta^{\ddagger}G_a/RT} - FB_c[\text{Ox}]e^{-\Delta^{\ddagger}G_c/RT}$$

$$\Delta^{\ddagger}G_c = \Delta^{\ddagger}G_c(0) + \alpha F \Delta\phi$$

$$\Delta^{\ddagger}G_a = \Delta^{\ddagger}G_a(0) - (1 - \alpha)F \Delta\phi$$

$$j = FB_a[\text{Red}]e^{-\Delta^{\ddagger}G_a(0)/RT}e^{(1-\alpha)F \Delta\phi/RT} - FB_c[\text{Ox}]e^{-\Delta^{\ddagger}G_c(0)/RT}e^{-\alpha F \Delta\phi/RT}$$

When the overpotential is large but negative (in practice, $\eta < -0.12$ V), corresponding to the cathode in electrolysis, the first exponential in eqn above may be neglected. Then $j = -j_0 e^{-\alpha f \eta}$

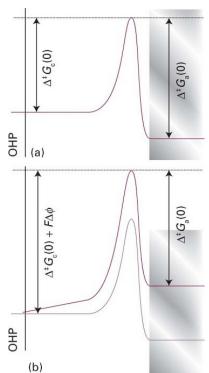


Figure 22.38 When the transition state resembles a species that has undergone reduction, the activation Gibbs energy for the anodic current is almost unchanged, but the transition state is the cathodic current. (a) Zero potential difference; (b) nonzero potential difference.

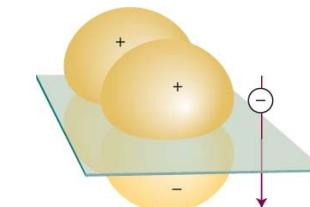


Fig. 6.10. Reflection in a plane through the nuclei of a linear molecule converts an orbital with angular momentum quantum number $m > 0$ (ψ^+) into its degenerate partner with $m < 0$ (ψ^-) and vice versa.

Good luck!