

University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 363
Paper Title:	Physical Chemistry

Time Allowed: THREE HOURS

Number of pages: TEN

This paper is divided into TWO sections.

Answer BOTH questions in SECTION A.

Answer **THREE** questions from SECTION B.

All questions are of equal value.

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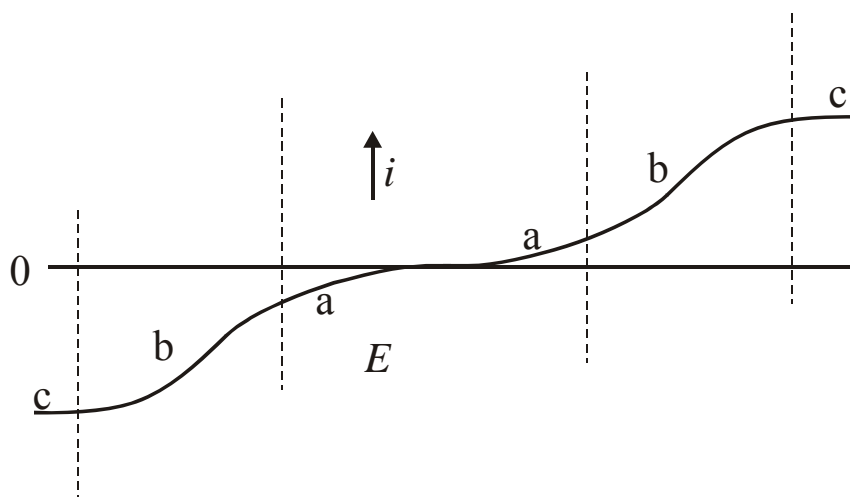
SECTION A

(Answer **BOTH** questions in this section)

1. The Butler-Volmer equation may be useful for this question.

$$i = i_0 \left(\exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \exp\left(\frac{-\alpha nF\eta}{RT}\right) \right)$$

- (a) State the conditions under which the Butler-Volmer equation holds.
- (b) Account for the shape of the experimental steady-state i vs E curve shown below. You may wish to refer to the three regions a, b and c.



- (c) Sketch the $\log |i|$ vs η plot (the Tafel plot) for the curve above. Indicate the regions a - c and comment, in detail, on the form of the plot in each region. Explain how kinetic information may be obtained from the Tafel plot.
- (d) On a single diagram sketch cyclic voltammograms for an electrochemically reversible redox couple and a quasi-reversible couple obtained using the same experimental conditions. Assume the reaction is $R \rightarrow O + e^-$, $\alpha = 0.5$ and equal concentrations for each couple. Account for the shape of the reversible voltammogram and for the differences seen between the reversible and the quasi-reversible systems. Note it is only necessary to consider the forward scans of the voltammograms in detail.

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2. [All parts of the following are worth equal marks.]

Write notes on *all* of the following:

- (a) The Carothers equation;
- (b) The Mayo equation;
- (c) The copolymer composition equation;
- (d) The steady-state rate law for free-radical polymerization;
- (e) The equation $n_i = F_n U^{i-1} (1-U) + (1-F_n)(i-1)U^{i-2}(1-U)^2$.

SECTION B

(Answer **THREE** questions from this section).

3. (a) In one dimension, the potential energy of a simple harmonic oscillator is:

$$V(x) = \frac{1}{2} k(x-x_0)^2,$$

where k is the force constant, and x_0 is also a constant.

Use Lagrange's equation of motion to **derive** a differential equation that could be solved to obtain $x(t)$. Do not solve the differential equation

- (b) **Show** that $[p_x^2, x] \neq 0$, in quantum mechanics. **What** is the significance of the result?
- (c) In deriving the expressions for the first-order corrections to the energy and the wave-function in non-degenerate perturbation theory, we write:

$$\psi_n^{(1)} = \sum_i c_i \psi_i^{(0)},$$
 where $\psi_i^{(0)}$ is an eigenfunction of $H^{(0)}$. **Define** the term $H^{(0)}$. **Why** is this expression exact?
- (d) (i) **Show** that the π energy levels in the Hückel approximation for the allyl radical ion ($\text{CH}_2\text{CHCH}_2^+$) are $E = \alpha$, and $\alpha \pm \sqrt{2} \beta$.
- (ii) **How** are the constants, α and β defined?
- (iii) **Explain** how would you obtain the molecular orbital coefficients?
- (e) **Show** that $L^2 = L_-L_+ + \hbar L_z + L_z^2$, where L is the orbital angular momentum operator.

4. (a) Provide definitions of the following terms as they apply to molecular symmetry and group theory:

- (i) principal symmetry axis;
- (ii) totally symmetric irrep;
- (iii) identity operation;
- (iv) Abelian point group.

(b) The equation for reducing a representation to a direct sum of irreps is:

$$a_q = \frac{1}{h} \sum_R n_R \chi(R) \chi_q(R) \quad (1)$$

Define all of the symbols in this equation.

(c) Methane has tetrahedral (T_d) symmetry, for which the character table is:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	$(x, y, z), (xy, xz, yz)$

Using this table, give the reduced forms (*i.e.* the direct sum of irreps) for the representations of the following bases:

- (i) Cartesian basis (Γ_{Cart})
 - (ii) rotation basis (Γ_{rot})
- (d) From your results in (c) and using equation (1), show that, for CH_4
- (i) $\Gamma_{3N} = A_1 \oplus E \oplus T_1 \oplus 3T_2$
 - (ii) $\Gamma_{\text{vib}} = A_1 \oplus E \oplus 2T_2$

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Question 4 continued

- (e) By drawing an appropriate diagram, define an internal-coordinate basis for the **stretching** modes of methane. Use this basis and the T_d character table to show (*without using equation (1)*) that

$$\Gamma_{\text{str}} = A_1 \oplus T_2$$

Hence show

$$\Gamma_{\text{bend}} = E \oplus T_2$$

5. (a) Define the electrochemical term $E^{\circ'}$
- (b) What is an electrochemically reversible redox system? Explain why such systems are also described as 'Nernstian'.
- (c) Answer the following assuming the couple O/R is electrochemically reversible.
- (i) With reference to concentration gradients, explain:
- (A) why the limiting currents of steady-state voltammograms obtained using a rotating disk electrode increase with electrode rotation rate; and
- (B) why the limiting currents of steady-state voltammograms obtained using a rotating disk electrode do not depend on potential scan rate, when the scan rate is below $\sim 50 \text{ mV s}^{-1}$. How and why does the voltammogram change when the scan rate is increased above 50 mV s^{-1} ?
- (ii) Sketch a steady-state voltammogram for a solution in which $[O] = 0.5[R]$. Label the voltammogram to indicate the anodic and cathodic currents, $E_{1/2}$ and E_e .
- (iii) Use the general voltammetric wave equation (shown below) to show that for a steady-state voltammogram, $E_{1/2} = E^{\circ'}$ (assuming $D_o = D_R$).

$$E = E^{\circ'} + \frac{RT}{nF} \ln \left(\frac{i - i_{l,c}}{i_{l,a} - i} \right)$$

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6. Consider the following statement about polymer produced by free-radical polymerization:

“In weight fraction distributions for **100% combination termination** and for **100% disproportionation termination**, the molecular weight of the peak maximum is equal to the number-average molecular weight.”

For **EACH** of the **TWO** indicated cases of free-radical polymerization:

- Give an expression for the number-molecular weight distribution (normalized or unnormalized) in terms of the probability of propagation.
- Hence obtain an expression for the number-molecular weight distribution (normalized or unnormalized) in the so-called ‘long-chain limit’.
- Derive an expression for the number-average molecular weight in terms of the parameters of your answer to (b).
- Also use your answer to (b) to obtain an expression for the weight-molecular weight distribution (normalized or unnormalized).
- Now prove the above statement.

Useful information:
$$\int_0^{\infty} \exp(-kM) \, dM = \frac{1}{k}$$

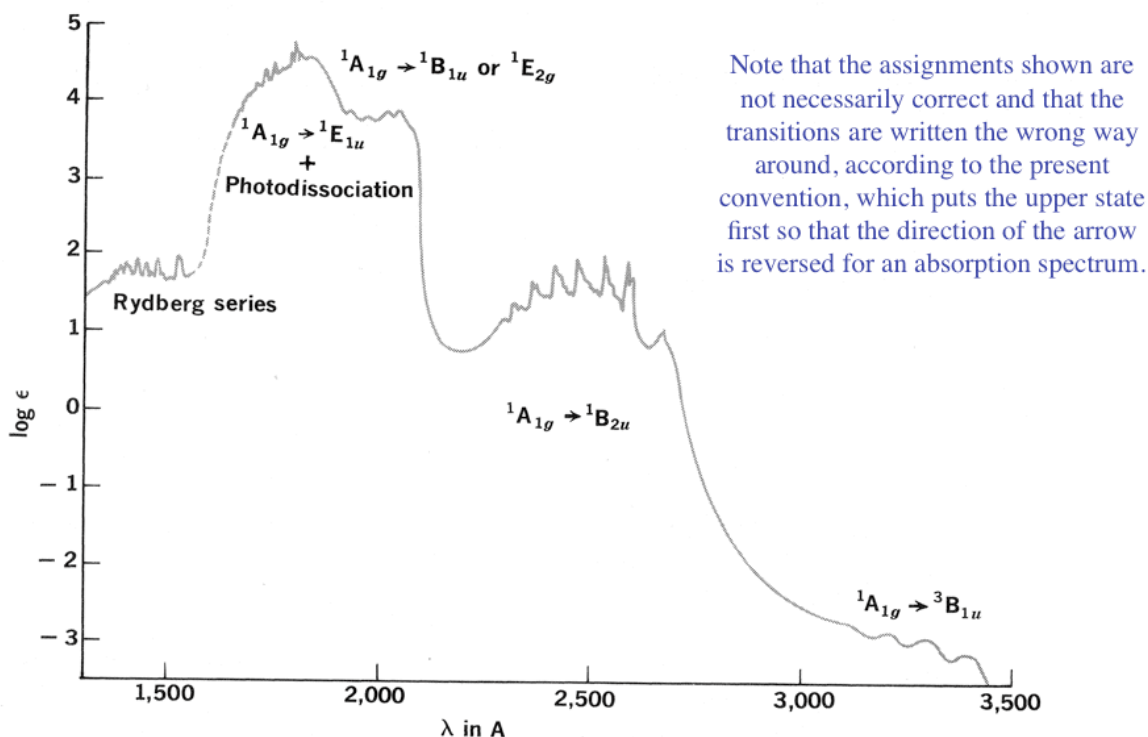
$$\int_0^{\infty} M \exp(-kM) \, dM = \frac{1}{k} \int_0^{\infty} \exp(-kM) \, dM$$

$$\int_0^{\infty} M^2 \exp(-kM) \, dM = \frac{2}{k} \int_0^{\infty} M \exp(-kM) \, dM$$

7. (a) Discuss the spectroscopic assignments shown for benzene in the diagram below.
- (b) Explain why the nominally forbidden transition at around 250 nm (2500 Å) occurs with significant intensity, and assign the vibrational peaks.
- (c) Suggest how the singlet-triplet transition near 350 nm might be observed.
- (d) Explain why a transition ${}^1A_{1g} \rightarrow {}^1A_{2u}$ is not observed in the spectrum.

A low-resolution spectrum of benzene

FIG. 11-10 The absorption spectrum of benzene in the ultraviolet spectral region. (From K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N.J., 1953.)



Benzene π -orbitals: The ground-state configuration is $a_{2u}^2 e_{1g}^4$ so ground-state is ${}^1A_{1g}$. The lowest excited state configuration $a_{2u}^2 e_{1g}^3 e_{2u}$ gives rise to singlet and triplet states of species B_{1u} , B_{2u} and E_{1u} . The ${}^1E_{1u}$ state is accessible by an allowed transition from ${}^1A_{1g}$.

(See the D_{6h} character table on the next page.)

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Question 7 continued

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_6$	$2S_3$	σ_h	$3\sigma_d$	$3\sigma_v$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	
B_{1g}	1	-1	1	-1	1	-1	1	1	-1	-1	1	-1	
B_{2g}	1	-1	1	-1	-1	1	1	1	-1	-1	-1	1	
E_{1g}	2	1	-1	-2	0	0	2	-1	1	-2	0	0	(R_x, R_y) (yz, zx)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0	(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	1	-1	1	-1	1	-1	-1	-1	1	1	-1	1	
B_{2u}	1	-1	1	-1	-1	1	-1	-1	1	1	1	-1	
E_{1u}	2	1	-1	-2	0	0	-2	1	-1	2	0	0	(x, y)
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0	

END OF PAPER