L-Università ta' Malta

Department of Chemistry
Faculty of Science

B.Sc. (Hons.) Year I

Sample Examination Paper I

CHE1217: Additional Techniques of Chemical Calculations — *n*th June 20XX, 08:30–10:35

Instructions

Read the following instructions carefully.

- Attempt only **TWO** questions.
- Each question carries **50** marks. The maximum mark is **100**.
- A list of mathematical formulae is provided on page 2.
- Only the use of non-programmable calculators is allowed.

MATHEMATICAL FORMULÆ

ALGEBRA

Factors

$$a^3 + b^3 = (a+b)(a^2 - ab + b^2)$$
$$a^3 - b^3 = (a-b)(a^2 + ab + b^2)$$

Quadratics

If $ax^2 + bx + c$ has roots α and β,

$$\Delta = b^2 - 4ac$$
$$\alpha + \beta = -\tfrac{b}{a} \qquad \alpha\beta = \tfrac{c}{a}$$

Finite Series

$$\sum_{k=1}^{n} 1 = n \qquad \sum_{k=1}^{n} k = \frac{n(n+1)}{2}$$
$$\sum_{k=1}^{n} k^2 = \frac{k(k+1)(2k+1)}{6}$$
$$(1+x)^n = \sum_{k=0}^{n} \binom{n}{k} x^n$$
$$= 1 + nx + \tfrac{n(n-1)}{2\cdot 1} x^2 + \cdots + x^n$$

GEOMETRY & TRIGONOMETRY

Distance Formula

If $A = (x_1, y_1)$ and $B = (x_2, y_2)$,

$$d(A,B) = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2}$$
$$= \sqrt{\Delta x^2 + \Delta y^2}$$

Pythagorean Identity

$$\cos^2\theta + \sin^2\theta = 1$$

General Solutions

$$\cos\theta = \cos\alpha \iff \theta = \pm\alpha + 2\pi\mathbb{Z}$$
$$\sin\theta = \sin\alpha \iff \theta = (-1)^n\alpha + \pi n,\ n \in \mathbb{Z}$$
$$\tan\theta = \tan\alpha \iff \theta = \alpha + \pi\mathbb{Z}$$

CALCULUS

Derivatives

$f(x)$	$f'(x)$
x^n	nx^{n-1}
$\sin x$	$\cos x$
$\cos x$	$-\sin x$
$\tan x$	$\sec^2 x$
$\cot x$	$-\operatorname{cosec}^2 x$
$\sec x$	$\sec x \tan x$
$\operatorname{cosec} x$	$-\operatorname{cosec} x \cot x$
e^x	e^x
$\log x$	$1/x$
uv	$u'v + uv'$
u/v	$(u'v - uv')/v^2$

Integrals

$f(x)$	$\int f(x)\,dx$
$x^n\ (n \neq -1)$	$\frac{x^{n+1}}{n+1}$
$\sin x$	$-\cos x$
$\cos x$	$\sin x$
$\tan x$	$\log(\sec x)$
$\cot x$	$\log(\sin x)$
$\sec x$	$\log(\sec x + \tan x)$
$\operatorname{cosec} x$	$\log(\tan \frac{x}{2})$
e^x	e^x
$1/x$	$\log x$
$\frac{1}{a^2+x^2}$	$\frac{1}{a}\tan^{-1}\left(\frac{x}{a}\right)$
$\frac{x}{\sqrt{a^2+x^2}}$	$\sin^{-1}\left(\frac{x}{a}\right)$

Homogeneous Linear Second Order ODEs

If the roots of $ak^2 + bk + c$ are k_1 and k_2, then the differential equation $ay'' + by' + cy = 0$ has general solution

$$y(x) = \begin{cases} c_1 e^{k_1 x} + c_2 e^{k_2 x} & \text{if } k_1 \neq k_2 \\ c_1 e^{kx} + c_2 x e^{kx} & \text{if } k = k_1 = k_2 \\ e^{\alpha x}(c_1 \cos\beta x + c_2 \sin\beta x) & \text{if } k = \alpha \pm \beta i \in \mathbb{C} \end{cases}$$

Infinite Series

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} = 1 + x + \frac{x^2}{2} + \frac{x^3}{3!} + \frac{x^4}{4!} \cdots$$
$$\cos x = \sum_{\substack{n=0 \\ n \text{ even}}}^{\infty} \frac{(-1)^{\frac{n}{2}}}{n!} x^n = 1 - \frac{x^2}{2} + \frac{x^4}{4!} - \cdots$$
$$\sin x = \sum_{\substack{n=1 \\ n \text{ odd}}}^{\infty} \frac{(-1)^{\frac{n-1}{2}}}{n!} x^n = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \cdots$$
$$\log(1+x) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n} x^n = x - \frac{x^2}{2} + \frac{x^2}{3} - \cdots, \quad x \in (-1, 1]$$

⚠ Attempt only **TWO** questions.

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1. (a) A function $f(x,y)$ is said to be separable if it can be expressed as a product $X(x)Y(y)$, where X is a function of x alone, and Y is a function of y alone.

If $f(x,y)$ is separable, show that:

(i) $\dfrac{\partial f}{\partial x} = \dfrac{dX}{dx}Y(y)$, (ii) $\dfrac{\partial f}{\partial y} = X(x)\dfrac{dY}{dy}$,

(iii) $\dfrac{\partial^2 f}{\partial x \partial y} = \left(\dfrac{dX}{dx}\right)\left(\dfrac{dY}{dy}\right)$, (iv) $\nabla^2 f = \dfrac{d^2 X}{dx^2}Y(y) + X(x)\dfrac{d^2 Y}{dy^2}$.

(b) The function $F(x,y,z)$ satisfies

$$\frac{\partial F}{\partial x} = 2x\sin y + z, \qquad \frac{\partial F}{\partial y} = x^2\cos y + \tan z, \qquad \frac{\partial F}{\partial z} = x + y\sec^2 z.$$

Given that $F(0,0,0) = 1$, determine $F(x,y,z)$.

(c) Suppose $f(x,y)$ is separable, and that

$$\frac{\partial f}{\partial x} + (y+1)\cos x \frac{\partial f}{\partial y} = 0.$$

Determine the particular solution, given the conditions $f(0,0) = 1$, and $f(0,3) = \frac{1}{2}$.

(d) The Schrödinger equation for a particle of mass m moving in the two-dimensional xy-plane is

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = E\Psi,$$

where $\hbar$ and E are constants, and $\Psi = \Psi(x,y)$ is the wave function.

Assuming the solutions is separable, and that $X(0) = Y(0) = X(a) = Y(b) = 0$, show that

$$\Psi(x,y) = C\sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{b}y\right),$$

where m, n are integers, and C is a real constant.

[12, 10, 12, 16 marks]

2. Consider the system of equations $\mathbf{A}\boldsymbol{x} = \boldsymbol{b}$, where $\boldsymbol{x} = (x, y, z)$,

$$\mathbf{A} = \begin{pmatrix} 1 & -2 & 2 \\ 2 & 5 & a \\ 2 & 3 & 0 \end{pmatrix}, \qquad \text{and} \qquad \boldsymbol{b} = \begin{pmatrix} 1 \\ 6 \\ b \end{pmatrix}.$$

(a) (i) For which values of a does $\mathbf{A}^{-1}$ exist? Find $\mathbf{A}^{-1}$ in terms of a for these values.

(ii) Solve the system when $a = -1$ and $b = 5$.

(iii) Solve the system when $a = -\frac{8}{7}$, and distinguish the different cases for b.

(b) For this part of the question, assume that $\mathbf{A}$ has $a = -2$.

(i) Determine the eigenvalues of $\mathbf{A}$.

(ii) Express $\mathbf{A}$ in the form $\mathbf{PDP}^{-1}$, where $\mathbf{D}$ is a diagonal matrix.

(iii) Solve the recurrence $\boldsymbol{x}_n = \mathbf{A}\boldsymbol{x}_{n-1}$, given that $\boldsymbol{x}_0 = (1, 1, 1)$.

[25, 25 marks]

3. (a) An explosion is modelled by the following pair of differential equations. Molecule A and B have concentration $x(t)$ and $y(t)$ at time t, respectively.

$$\dot{x} = x + 3y$$
$$\dot{y} = x$$

Let $\alpha = \frac{1}{2}(1 + \sqrt{13})$.

(i) Express the equations as a matrix differential equation.

(ii) By diagonalising the appropriate matrix, solve the differential equations for $x(t)$ and $y(t)$.

[Hint: Use α in your working to keep thing simple. Also, notice that $1 - \alpha = -\frac{3}{\alpha} = \frac{1}{2}(1 - \sqrt{13})$.]

(b) Determine the matrix $\mathbf{R}$ which corresponds to a rotation in three dimensional space of ϑ (anticlockwise) around the y-axis. Prove that $\det(\mathbf{R}) = 1$, and interpret this geometrically.

[35, 15 marks]

Solutions

1. (a) Use the product rule from differentiation for all of these, and note that some partial derivatives will be zero.

   (b) $F(x,y,z) = x^2 \sin y + y \tan z + xz + 1$.

   (c) The general solution is $f(x,y) = \left(A\frac{e^{\sin x}}{y+1}\right)^C$, and the conditions gives us $A = 1$ and $C = \frac{1}{2}$, so the particular solution is $f(x,y) = \sqrt{\frac{e^{\sin x}}{y+1}}$.

   (d) Standard theory.

   By part (a), assuming $\Psi = XY$, the equation is just

$$\frac{d^2X}{dx^2}Y + X\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2}\Psi,$$

   and dividing through by $\Psi = XY$, we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE}{\hbar^2}.$$

   Thus we have

$$\frac{1}{X}\frac{d^2X}{dx^2} = -C_1 \qquad \text{and} \qquad \frac{1}{Y}\frac{d^2Y}{dy^2} = -C_2$$

   where $C_1 + C_2 = 2mE/\hbar^2$. In other words,

$$X'' + C_1X = 0 \qquad \text{and} \qquad Y'' + C_2Y = 0.$$

   These are second order differential equations with constant coefficients, which can be solved using the methods from CHE1215 (working must be shown!), and they have solutions

$$X = A\sin(\sqrt{C_1}x) \qquad \text{and} \qquad Y = B\sin(\sqrt{C_2}y)$$

   respectively (notice the boundary conditions $X(0) = Y(0) = 0$ give the forms above).

   Moreover, since $X(a) = 0$, we have $\sin(\sqrt{C_1}a) = 0$, so we must have $\sqrt{C_1}a = m\pi$ for some m, i.e., $\sqrt{C_1} = m\pi/a$. Similarly, since $Y(b) = 0$, we get that $\sqrt{C_2} = n\pi/b$ for some integer n.

   Thus, relabelling AB with C, we get

$$\Psi = XY = C\sin\left(\frac{m\pi}{a}x\right)\sin\left(\frac{n\pi}{b}y\right).$$

2. (a) (i) We have $\det(\mathbf{A}) = -7a - 8$, so $\mathbf{A}^{-1}$ exists so long as $a \neq -\frac{8}{7}$.

$$\mathbf{A}^{-1} = \frac{1}{7a+8}\begin{pmatrix} 3a & -6 & 2(a+5) \\ -2a & 4 & a-4 \\ 4 & 7 & -9 \end{pmatrix}.$$

(ii) $\boldsymbol{x} = \mathbf{A}^{-1}\boldsymbol{b} = (1,1,1)$, i.e., $x = y = z = 1$.

(iii) When $a = -\frac{8}{7}$, we get two cases: If $b = \frac{46}{9}$, then the system is consistent and we have the following infinite family of solutions: $x = \lambda$, $y = \frac{46}{27} - \frac{2}{3}\lambda$ and $z = \frac{119}{54} - \frac{7}{6}\lambda$ for any $\lambda \in \mathbb{R}$.

If $b \neq \frac{46}{9}$, then there are no solutions.

(b) (i) The characteristic polynomial is $\chi_{\mathbf{A}}(\lambda) = \lambda^3 - 6\lambda^2 + 11\lambda - 6 = (\lambda-1)(\lambda-2)(\lambda-3)$, so the eigenvalues are $1, 2, 3$.

(ii) Determining eigenvectors for each eigenvalue, we can take

$\lambda = 1 \implies \boldsymbol{x} = (1,-1,-1)$

$\lambda = 2 \implies \boldsymbol{x} = (2,-2,-1)$

$\lambda = 3 \implies \boldsymbol{x} = (0,1,1)$

and so if we let $\mathbf{P} = \begin{pmatrix} 1 & 2 & 0 \\ -1 & -2 & 1 \\ -1 & -1 & 1 \end{pmatrix}$, then $\mathbf{A} = \mathbf{PDP}^{-1}$, where $\mathbf{D}$ is a diagonal matrix with $1, 2, 3$ on the main diagonal.

(iii) $\boldsymbol{x}_n = \mathbf{A}^n \boldsymbol{x}_0$, so we just need to work out $\mathbf{A}^n$. Using the diagonal form,

$$\begin{aligned} \mathbf{A}^n &= (\mathbf{PDP}^{-1})(\mathbf{PDP}^{-1})\cdots(\mathbf{PDP}^{-1}) \\ &= \mathbf{PD}(\mathbf{P}^{-1}\mathbf{P})\mathbf{D}(\mathbf{P}^{-1}\mathbf{P})\cdots(\mathbf{P}^{-1}\mathbf{P})\mathbf{DP}^{-1} \\ &= \mathbf{PD}^n\mathbf{P}^{-1} \\ \implies \mathbf{A}^n\boldsymbol{x}_0 &= \begin{pmatrix} 1 & 2 & 0 \\ -1 & -2 & 1 \\ -1 & -1 & 1 \end{pmatrix}\begin{pmatrix} 1 & & \\ & 2^n & \\ & & 3^n \end{pmatrix}\begin{pmatrix} 1 & 2 & -2 \\ 0 & -1 & 1 \\ 1 & 1 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \\ \therefore \quad \boldsymbol{x}_n &= \begin{pmatrix} 1 \\ 2 \times 3^n - 1 \\ 2 \times 3^n - 1 \end{pmatrix}. \end{aligned}$$

3. (a) (i) The given differential equations are equivalent to the matrix equation $\dot{\boldsymbol{x}} = \mathbf{A}\boldsymbol{x}$, where $\boldsymbol{x} = \boldsymbol{x}(t) = (x(t), y(t))$, and $\mathbf{A} = \left(\begin{smallmatrix} 1 & 3 \\ 1 & 0 \end{smallmatrix}\right)$.

(ii) The matrix has eigenvalues α and $1-\alpha$, and corresponding eigenvectors $(\alpha, 1)$ and $(1-\alpha, 1)$, so we can express $\mathbf{A}$ as

$$\mathbf{A} = \mathbf{P}\begin{pmatrix} \alpha & \\ & 1-\alpha \end{pmatrix}\mathbf{P}^{-1}, \qquad \text{where } \mathbf{P} = \begin{pmatrix} \alpha & 1-\alpha \\ 1 & 1 \end{pmatrix}.$$

Thus, the equation we have is $\dot{\boldsymbol{x}} = \mathbf{PDP}^{-1}\boldsymbol{x}$, or equivalently, $\mathbf{P}^{-1}\dot{\boldsymbol{x}} = \mathbf{DP}^{-1}\boldsymbol{x}$. If we let $\boldsymbol{u} = \mathbf{P}^{-1}\boldsymbol{x}$, then this is $\dot{\boldsymbol{u}} = \mathbf{D}\boldsymbol{u}$, i.e.,

$$\begin{pmatrix} u'(t) \\ v'(t) \end{pmatrix} = \begin{pmatrix} \alpha u(t) \\ -\frac{3}{\alpha} v(t) \end{pmatrix}.$$

In general, the differential equation $f'(t) = af(t)$ is equivalent to $\frac{f'(t)}{f(t)} = a$, and integrating both sides with respect to t, we get $\log(f(t)) = at + \log c$, i.e., $f(t) = c\, e^{at}$. So the vector differential equation above becomes

$$\begin{pmatrix} u(t) \\ v(t) \end{pmatrix} = \begin{pmatrix} Ae^{\alpha t} \\ Be^{-3t/\alpha} \end{pmatrix},$$

and thus we've determined the solution $\boldsymbol{u}(t)$ of $\dot{\boldsymbol{u}} = \mathbf{D}\boldsymbol{u}$. Now to translate this into the desired solution $\boldsymbol{x}(t)$ of the original equation, we use the fact that $\boldsymbol{x} = \mathbf{P}\boldsymbol{u}$:

$$\boldsymbol{x}(t) = \mathbf{P}\boldsymbol{u}(t) = \begin{pmatrix} A\alpha e^{\alpha t} + B(1-\alpha)e^{-3t/\alpha} \\ Ae^{\alpha t} \qquad\qquad + Be^{-3t/\alpha} \end{pmatrix},$$

i.e., the solution is

$$\begin{cases} x(t) = A\alpha e^{\alpha t} + B(1-\alpha)e^{-3t/\alpha} \\ y(t) = Ae^{\alpha t} + Be^{-3t/\alpha}. \end{cases}$$

(b) Since the y-axis is the axis of revolution, then $\mathbf{R}$ leaves $\boldsymbol{j}$ fixed, i.e., $\mathbf{R}\boldsymbol{j} = (0, 1, 0)$.

For $\boldsymbol{j}$ and $\boldsymbol{k}$, if we recall the standard matrix $\left(\begin{smallmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{smallmatrix}\right)$ for rotations in the 2D plane, we see that this is what occurs to $\boldsymbol{i}$ and $\boldsymbol{j}$ in xz-plane, while retaining their y coordinates, so $\mathbf{R}\boldsymbol{i} = (\cos\theta, 0, \sin\theta)$ and $\mathbf{R}\boldsymbol{k} = (-\sin\theta, 0, \cos\theta)$.

Thus

$$\mathbf{R} = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix}.$$

For the determinant, we expand along the middle row and column:

$$\det(\mathbf{R}) = \begin{vmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{vmatrix} = +1 \cdot \begin{vmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{vmatrix} = \cos^2\theta + \sin^2\theta = 1,$$

which makes sense, since geometrically, what the determinant represents is the scale factor by which volume is multiplied when the transformation **R** is carried out (which is 1, since volumes do not change when regions are simply being rotated).