IMPERIAL COLLEGE LONDON

BSc and MSci DEGREES – MAY 2013, for Internal Students of the Imperial College of Science, Technology and Medicine

This paper is also taken for the relevant examination for the Associateship

ADVANCED CHEMISTRY THEORY IIIB

Paper 2

Friday 10th May 2013, 14:00-16:15

PLEASE NOTE THAT IT IS DEPARTMENTAL POLICY THAT THESE EXAM QUESTIONS MAY REQUIRE UNDERSTANDING OF ANY PRIOR CORE COURSE.

USE A SEPARATE ANSWER BOOK FOR EACH QUESTION. WRITE YOUR CANDIDATE NUMBER ON EACH ANSWER BOOK.
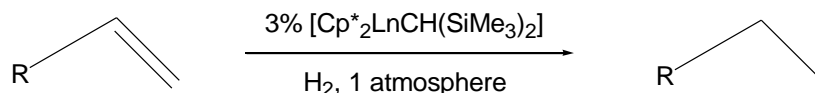
3.I7 – Lanthanides and Actinide Chemistry

Answer parts a), b), c) **AND** d) and **EITHER** part e) **OR** f) of this question.

a) For the Tm^{3+} ion, determine (i) the Russell-Saunders ground state term and (ii) its magnetic moment.

(5 marks)

b) For the catalytic hydrogenation reaction shown below, give a reaction mechanism identifying the individual reaction steps involved.
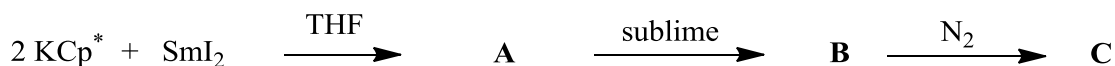
$$R \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown \quad \xrightarrow[\text{H}_2,\ 1\ \text{atmosphere}]{3\%\ [\text{Cp*}_2\text{LnCH(SiMe}_3)_2]} \quad R \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown$$

(5 marks)

c) Uranocene, $[U(\eta^8\text{-}C_8H_8)_2]$, is a stable, symmetric sandwich complex that has no direct counterpart in transition metal chemistry. Using simple molecular orbital representations, discuss this statement.

(5 marks)

d) Identify and illustrate the lanthanide-containing products **A**, **B** and **C** in the following reactions:

$$2\ KCp^* \ +\ SmI_2 \quad \xrightarrow{\text{THF}} \quad \mathbf{A} \quad \xrightarrow{\text{sublime}} \quad \mathbf{B} \quad \xrightarrow{N_2} \quad \mathbf{C}$$

(6 marks)

e) Discuss the role of (i) lanthanide ions in 'self-cleaning ovens' and (ii) actinide ions in commercial smoke detectors.

(4 marks)

f) Identify and draw the structures of the metal-containing products **D** and **E** in the following reactions:

i) $ThCl_4$ + excess $Na(C_5H_5)$ $\longrightarrow$ **D**

ii) $ZrCl_4$ + excess $Na(C_5H_5)$ $\longrightarrow$ **E**
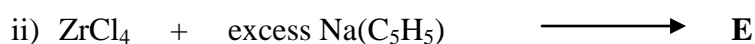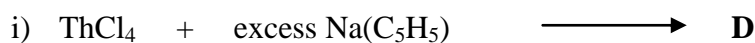
(4 marks)

3I.8 – Solvents and Solvent Effects

Answer part a) and **EITHER** part b) **OR** part c) of this question.

a) Kosower's Z scale is based upon the energy of the longest absorption wavelength transition of a charge transfer within N-ethyl-4-carboxymethylpyridinium iodide, shown below.
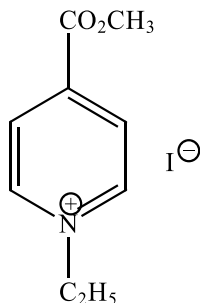
Answer **ALL** parts below:

   i)   Draw the excited state of the charge transfer.

(2 marks)

   ii) Explain the solvatochromic trend in charge transfer energy values shown in the table below.

Solvent	Z (kcal mol^{-1})
Water	94.6
Ethanol	79.6
Acetonitrile	71.3
Acetone	65.5
Dichloromethane	64.7
Benzene	54.0

(3 marks)

   iii) Draw one diagram showing the free energy change for the charge transfer reaction in both a non-polar solvent and a polar solvent. Clearly label every ΔG.

(4 marks)

   iv) Reaction rate data for the synthesis of a new product were obtained in various solvents as shown in the table below. Use this data to obtain an LSER, using the Z parameter, which will predict the rate of this reaction in various solvents.

| Solvent	Z (kcal mol^{-1})	k_2 (min^{-1} M^{-1})
Water	94.6	238,000.00
Ethanol	79.6	2,640.00
Acetonitrile	71.3	219.00
Acetone	65.5	38.50
Dichloromethane	64.7	30.30
Benzene	54	1.22

(3 marks)

v) Using your equation from part (iv), predict the rate of reaction in ethyl acetate ($Z = 59.4$ kcal mol^{-1}) and in methanol ($Z = 83.6$ kcal mol^{-1}).

(2 marks)

vi) Z is a function of the Kamlet-Taft solvent parameters π^* and α. What interaction is most responsible for the α dependence?

(1 mark)

b) A remarkable solvent effect has been observed on the rotamer equilibrium of ethoxycarbonylmethylene triphenylphosphorane, shown below. (Snyder, *Tetrahedron Lett.* 1971, 4923.)
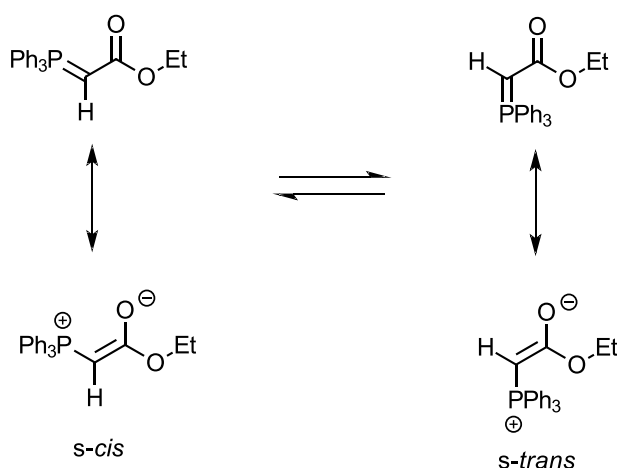
s-*cis*   s-*trans*

Equilibrium constants for this rotation have been measured in various solvents, as in the table below.

| Solvent	ε	K = [s-*cis*]/[s-*trans*]
Tetrachloromethane	2.2	6.2
Benzene	2.2	5.9
Nitromethane	35.0	2.4
Acetonitrile	36.0	2.3
Chloroform	4.8	1.8

Answer **ALL** parts below:

i) Explain the observed solvent effect on this rotational equilibrium.

(7 marks)

ii) Explain what would happen to this equilibrium if ethanol was added to one of the solvents.

(2 marks)

iii) If water is added to a solution containing the compound dissolved in acetonitrile, the UV-vis spectrum of the solution is shifted dramatically. Explain this phenomenon.

(1 mark)

c) You have discovered the extremely valuable nutraceutical product SWEETNESS®, the structure of which is shown below:
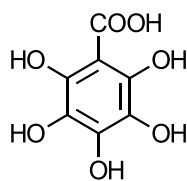
Answer **ALL** parts below:

You synthesized SWEETNESS® as an aqueous product mixture, and your supervisor has asked you to determine the best purification technique. You decide first to try extraction from water. Some possible extraction solvents and their properties are shown in the table below:

Solvent	α	β	π*	water solubility
Acetonitrile	0.19	0.66	0.66	miscible
Acetone	0.08	0.48	0.71	miscible
Chloroform	0.44	0	0.58	immiscible
Ethyl Acetate	0	0.45	0.55	immiscible
n-Hexane	0	0	-0.08	immiscible
Toluene	0	0.09	0.56	immiscible

i) What is the best extraction solvent for SWEETNESS® from the table? Briefly explain your choice.

(3 marks)

ii) Your supervisor ignores your recommendation and orders diethyl ether for the extraction. You therefore decide to precipitate SWEETNESS® out of the diethyl ether extract using an antisolvent. What is the best antisolvent in the table? Briefly explain your choice.

(2 marks)

iii) Your supervisor has now become obsessed with green solvents and has ordered you to re-run the synthesis in an ionic liquid. The synthesis now gives higher yields, but in order to recover the product you must now use a chromatography column with silica gel. Which of the solvents in the table will give SWEETNESS® the fastest elution time? Briefly explain your choice.

(1 mark)

iv) Your supervisor changes his mind and decides that the *slowest* elution time would be best. Which of the solvents on the list will give the slowest elution time?

(1 mark)

v) The column is far too slow, and you realize that this is because the ionic liquid your supervisor selected is a strong base. You decide to dissolve your SWEETNESS® mixture with the ionic liquid into water and use a new extraction solvent. Which is now the best extraction solvent in the table for this new aqueous solution? Briefly explain your choice.

(3 marks)

5

3.O7 – Polymers

Answer part a) and **EITHER** part b) **OR** part c) of this question.

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

   i) Give a brief definition of the following terms:
   - Fragile glass-former
   - heterotactic
   - anti-plasticisation

   (3 marks)

   ii) Explain how small angle X-ray scattering can be used to determine the degree of crystallinity in a polymer.

   (2 marks)

   iii) Describe the process of Ostwald ripening. What is the influence of kinetics on this process?
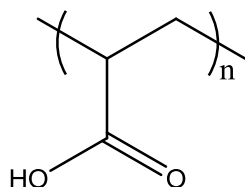
   (4 marks)

   iv) What is spinodal decomposition?

   (4 marks)

   v) The addition of Ca^{2+} ions to poly(acrylic acid) (below) causes a significant increase in viscosity. Explain this observation.

   (4 marks)

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

   i) What is the glass transition temperature? Explain why some polymers do not exhibit this transition.

   (4 marks)

   ii) Describe what information a radial distribution function of an amorphous solid can tell us. How can this be experimentally verified?

   (4 marks)

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

   i) Explain how solid state NMR spectroscopy can be used to determine the degree of crystallinity in a polymer.
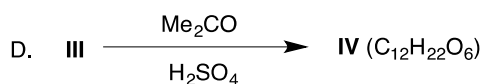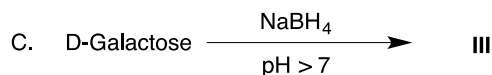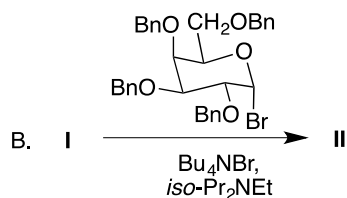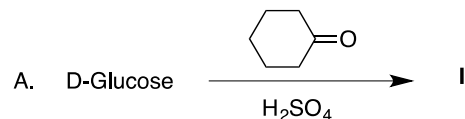
   (4 marks)

   ii) An inorganic aluminosilicate glass is quenched from the melt and afterwards it is annealed. Explain what role the group I and II cations play within the glass structure. What effect does the annealing have on the structure of the glass?
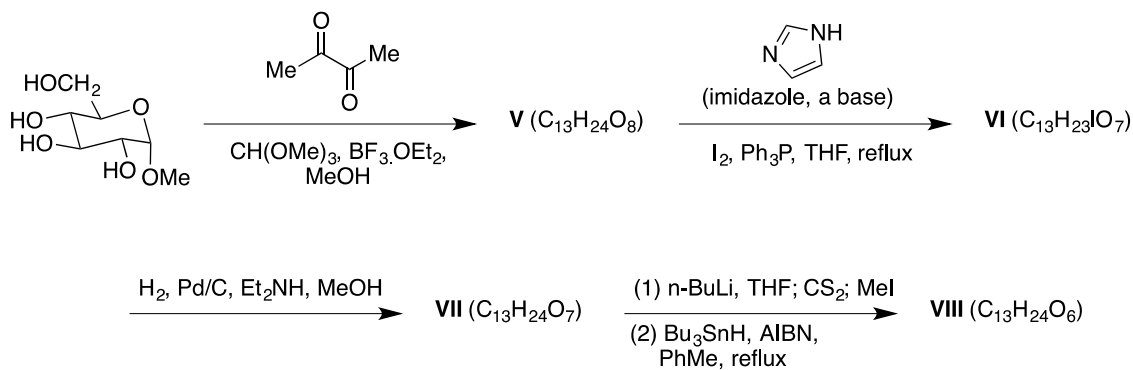
   (4 marks)

3.O8 – Carbohydrate Chemistry

Answer part a) **AND** either part b) **OR** part c) of this question.

a) Suggest structures for the products **I**, **II**, **III** and **IV** formed in all four transformations:

A. D-Glucose $\xrightarrow[\text{H}_2\text{SO}_4]{}$ **I**

B. **I** $\xrightarrow[\substack{\text{Bu}_4\text{NBr,} \\ \textit{iso}\text{-Pr}_2\text{NEt}}]{}$ **II**

C. D-Galactose $\xrightarrow[\text{pH} > 7]{\text{NaBH}_4}$ **III**

D. **III** $\xrightarrow[\text{H}_2\text{SO}_4]{\text{Me}_2\text{CO}}$ **IV** ($C_{12}H_{22}O_6$)

(4 marks each)

b) Suggest structures for the products **V**, **VI**, **VII** and **VIII** formed in the following sequence of transformations:

$\xrightarrow[\substack{\text{CH(OMe)}_3\text{, BF}_3\text{.OEt}_2, \\ \text{MeOH}}]{}$ **V** ($C_{13}H_{24}O_8$) $\xrightarrow[\substack{\text{(imidazole, a base)} \\ \text{I}_2\text{, Ph}_3\text{P, THF, reflux}}]{}$ **VI** ($C_{13}H_{23}IO_7$)

$\xrightarrow[]{\text{H}_2\text{, Pd/C, Et}_2\text{NH, MeOH}}$ **VII** ($C_{13}H_{24}O_7$) $\xrightarrow[\substack{\text{(2) Bu}_3\text{SnH, AIBN,} \\ \text{PhMe, reflux}}]{\text{(1) n-BuLi, THF; CS}_2\text{; MeI}}$ **VIII** ($C_{13}H_{24}O_6$)

Hint: hydrolysis of the final product **VIII** using aqueous trifluoroacetic acid gave methyl 2,6-di-deoxy-α-D-glucopyranoside (**IX**)

IX
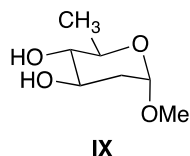
(9 marks)

c) Reaction of D-ribonolactone (**X**) with acetic anhydride and pyridine gave **XI** ($C_{11}H_{14}O_8$). Reaction of **XI** with DBU (**XII**), a strong non-nucleophilic base, gave **XIII** ($C_7H_6O_4$). Hydrogenation of **XIII** over palladium on calcium carbonate gave **XIV** ($C_7H_{10}O_4$). Suggest structures for all the unknown compounds and comment on the stereochemistry of the lactone **XIV**.

X   XII

(9 marks)

9
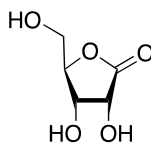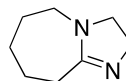
3.P7 – Lyotropics

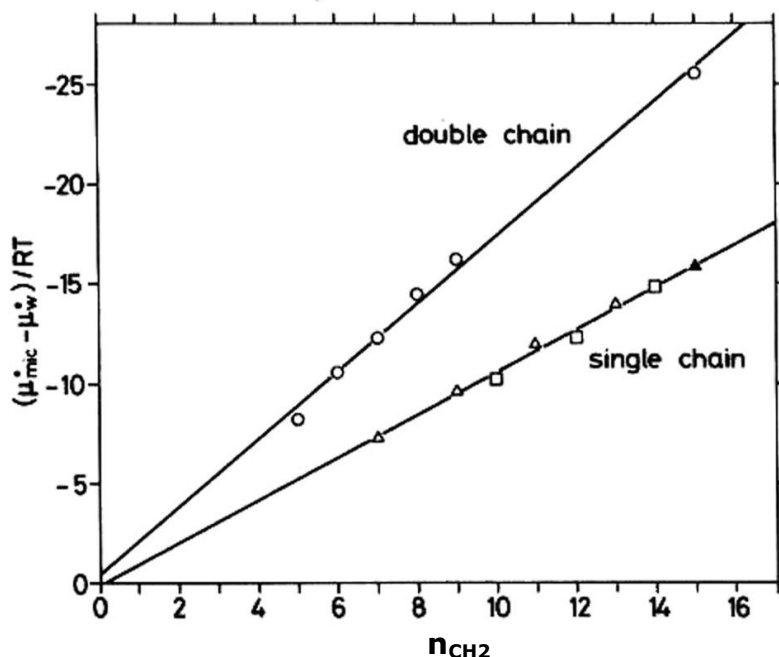Answer any **TWO** of the three parts a), b) and c) of this question.

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

Data for the free energy of micellization as a function of chainlength for a single-chain lipid and a double-chain lipid are plotted below.

i) Explain whether the data show that micellization is a spontaneous process for both lipids, at all chainlengths.

(2 marks)

ii) Explain why the plots are linear.

(2 marks)

iii) Estimate the free energy increment per CH_2 group for each lipid.

(3 marks)

iv) Explain why the increment per CH_2 group is different for the two lipids.

(2.5 marks)

v) Explain why both intercepts lie close to zero in the free energy.

(3 marks)

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

For a curved interface, the cross-sectional area $a(t)$ depends upon the distance t moved perpendicular to the interface according to:

$$a(t) = a_o \left[1 + 2Ht + Kt^2 \right]$$

i) Define all the terms on the right hand side of this equation, and state the expressions for H and K in terms of the principal radii of curvature c_1 and c_2.

(3.5 marks)

ii) For a spherical micelle of hydrophobic radius r, for a cylindrical micelle, and for a flat bilayer, deduce expressions for the change in interfacial area per molecule on moving from its value a_o at the polar headgroup – hydrocarbon chain interface, to the outside surface of each type of aggregate (i.e., t will correspond to the thickness of the headgroup region).

(6 marks)

iii) Calculate numerical values for the area per molecule a, at the surface of each type of aggregate, assuming $r = 2.8$ nm, $t = 0.5$ nm, and $a_o = 0.65$ nm^2.

(3 marks)

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

Using a micropipette of inner diameter 1×10^{-6} m in an aspiration experiment on a lipid bilayer vesicle of radius 2×10^{-5} m, the following data were recorded:

Δp / Pa	0	4.0×10^3	8.0×10^3	1.2×10^4
L_p / m	0	1.9×10^{-6}	4.1×10^{-6}	6.0×10^{-6}

i) Define Δp and L_p.

(2 marks)

ii) From these data, estimate the area compressibility modulus K_A, by applying the following equations (note that α is the area dilation $\Delta A / A_o$):

$$K_A \alpha = \sigma = \frac{\Delta p}{2} \left(\frac{R_p}{1 - R_p / R_s} \right); \qquad \Delta A = 2\pi R_p \left(1 - \frac{R_p}{R_s} \right) L_p$$

(10.5 marks)

11

3.P10 – Soft Condensed Matter

Answer part a) and **EITHER** part b) **OR** part c) of this question.

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

    i) What is viscoelasticity? With the help of an appropriate diagram explain the time dependent response of the shear strain in a viscoelastic material. Provide one example of a viscoelastic material.

                                          (4 marks)

    ii) The Young's modulus can be estimated from the energy density: $E \gg \dfrac{e}{a^3}$.

       Define ε and a in the equation above and show that this equation holds for an atomic crystal when the interatomic potential is given by:

$$u(r) = \varepsilon\left(\left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^6\right).$$

       Hint: you may assume that $a \sim \sigma$

                                          (5 marks)

    iii) Estimate the Young's modulus of a crystal consisting of colloidal particles at a density of 10^{21} colloids/m^3 and at 300 K. Assume that the characteristic interaction between the particles is of the order of 10 $k_B T$. Will this crystal be able to sustain a pressure of 10 Pa?

                                          (3 marks)

    iv) Sketch the DLVO potential as a function of intercolloidal distance. Explain how this potential responds to changes in the salinity of the solution, and indicate under which conditions the DLVO theory predicts stable dispersions, flocculation and coagulation.

                                          (3 marks)

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

The phase diagram below describes the coexistence behaviour of a liquid-liquid mixture.

    i) In what region of the phase diagram will nucleation take place? Justify your answer discussing the variation of the free energy with composition. Make use of appropriate diagrams to support your explanations.

                                          (2 marks)

ii) A fluid mixture undergoes de-mixing through a nucleation process. Assuming that the critical radius of the nucleating clusters is 1 nm, estimate the surface tension of the fluid-fluid interface and the height of the free energy barrier for nucleation.

Data: you can assume that the reduction in free energy per unit volume associated with the nucleation process is: -10^7 J/m^3

(3 marks)

iii) Using mean field theory, estimate the composition of the mixture on the spinodal line.

Data: T=300 K, $\chi = 3$, $\frac{\Delta F}{k_B T} = \chi x_a x_b + x_a \ln x_a + x_b \ln x_b$

(5 marks)

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

i) Consider a freely jointed chain with a degree of polymerization N and a segment-segment distance a. Show that the free energy associated with the extension, r, of the end-to-end distance from its equilibrium position is given by: $F(r) = \frac{3 k_B T r^2}{2 N a^2}$

Data: The probability distribution for the end-to-end distance is:

$$P(r, N) = C \exp\left(\frac{-3 r^2}{2 N a^2}\right)$$

(3.5 marks)

ii) The degree of polymerization of a polymer is $N=10^4$ and the segment-segment distance, 1 nm. Using the freely jointed chain model estimate the force that would have to be generated with an optical tweezer to obtain an end-to-end distance of 200 nm at 300 K.

(4.5 marks)

iii) Polymer excluded volume effects can have a significant impact on the polymer conformation. Briefly explain the physical origin of the excluded volume effects and how they modify the equilibrium end-to-end distance of the polymer as well as the scaling behaviour of this distance with the degree of polymerization.

(2 marks)

3.P12 – Advanced Electrochemistry

Answer part a) and **EITHER** part b) or part c) of this question.

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

In impedance spectroscopy, the concept of input, output and transfer functions is central.

   i) Give an example of an input function and a related output function and name the corresponding transfer function. Define all terms.

(3 marks)

   ii) The Laplace transforms of common input functions are given on the attached table (at the end of this question).

Calculate the admittance Y of A) a single resistor and B) a single capacitor.

(6 marks)

   iii) Draw a schematic of the Randles-Ershler circuit, in series with a solution resistance, and briefly explain the physical meaning of each circuit element. Show how you construct an expression for the total impedance of this nested circuit from the individual circuit elements based on electric circuit laws. Define the impedance of each circuit element in the frequency domain at the equilibrium potential.

(6 marks)

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

The impedance may be split formally into a real and an imaginary component: $Z_{tot} = Z_{real} + i \cdot Z_{im}$, where 'i' is the imaginary number. Suppose an electrochemical cell is accurately represented by a solution resistance R_s, in series with a double layer capacitance C_{dl}.

   i) Write down an expression for the total admittance $Y(\omega)$ of the system in the frequency domain. Derive an expression for $Y(\omega)$, where the real and imaginary parts are clearly separated.

(4 marks)

   ii) Sketch a Nyquist plot for the admittance of the above circuit. Indicate which information can be extracted from this plot. Briefly rationalize your suggestions, based on electric circuit laws or using the expressions for Y_{real} and Y_{im} derived in part i).

(6 marks)

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

An electrochemical cell contains an electrolyte solution and a dissolved redox species, which undergoes a redox reaction at a gold working electrode. The cell is at electrochemical equilibrium and the concentrations of reduced and oxidized species are the same.

   i) Assuming that the concentration impedances are negligible, sketch a simple equivalent circuit diagram and specify to which physical or chemical process each circuit element is related.

(4 marks)

   ii) Draw a Nyquist diagram for the impedance of this circuit and show how you extract the values for each of the circuit elements. Rationalize your conclusion on the basis of electric circuit laws, where possible.

(6 marks)

Additional sheet with common Laplace transforms (from the lecture notes):

$f(t)$	$F(s)$	$f(t)$	$F(s)$
1	$1/s$	$\sinh bt$	$\dfrac{b}{s^2 - b^2}$
t^n	$\dfrac{n!}{s^{n+1}}$	$\cosh bt$	$\dfrac{s}{s^2 - b^2}$
$e^{\alpha t}$	$\dfrac{1}{s - \alpha}$	$t\sin bt$	$\dfrac{2bs}{(s^2 + b^2)^2}$
$\sin bt$	$\dfrac{b}{s^2 + b^2}$	$t\cos bt$	$\dfrac{s^2 - b^2}{(s^2 + b^2)^2}$
$\cos bt$	$\dfrac{s}{s^2 + b^2}$	Step function $u(t)$ $f(t) = 1,\ t \geq 0$ $f(t) = 0,\ t < 0$	$\dfrac{1}{s}$
$t^n e^{-\alpha t}$	$\dfrac{n!}{(s + \alpha)^{n+1}}$	$\delta(t)$	1
$\ast f(t)\, e^{-\alpha t}$	$F(s+\alpha)$	$\delta(t - d)$	e^{-sd}