# University of Illinois at Chicago • CHEM 233
## Dr. Chad Landrie • Fall, 2009

# MIDTERM EXAM

Student Label

| FULL NAME | | Section Day/Time | |
|-----------|--|------------------|--|
| UIN | | Student Signature | |
| TA | | TA Signature | |

## Instructions:

1. Do not open or begin exam until instructed.

2. Check the label at the top of the exam. If all the information is correct, replicate that information in the table above. Also, enter your information on the top of each page once the exam begins. **One point** will be **subtracted** for each **missing entry on each page.**

3. Sign in the box labeled *Student Signature*. Ink only.

4. Place your UIC ID on your desktop. The instructor/TA will check your ID and sign your exam after time begins. Exams without a signature will not be graded.

5. When finished, return your exam to *your TA only*. Exams that are not returned to your TA, leave the room or are left in the general vicinity will not be graded.

## Policies:

1. No electronic devices, other than a calculator, may be used during the exam. Use of an electronic device other than a calculator, including cell phones, will result in immediate exam confiscation and failure. If it rings, let it ring.

2. All cases of academic dishonesty will be referred to the UIC Judiciary committee and pursued to the fullest extent.

3. For full credit, show all work and equations.

4. No exams will be accepted or graded that are turned in after time is called.

| | |
|---|---|
| **Page 2 (15 pts)** | |
| **Page 3 (15 pts)** | |
| **Page 4 (14 pts)** | |
| **Page 5 (14 pts)** | |
| **Page 6 (18 pts)** | |
| **Page 7 (14 pts)** | |
| **Page 8 (10 pts)** | |
| **Total Points (100)** | |

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

1.  Rank the items in each set below according to the trends observed for the physical or chemical properties indicated.
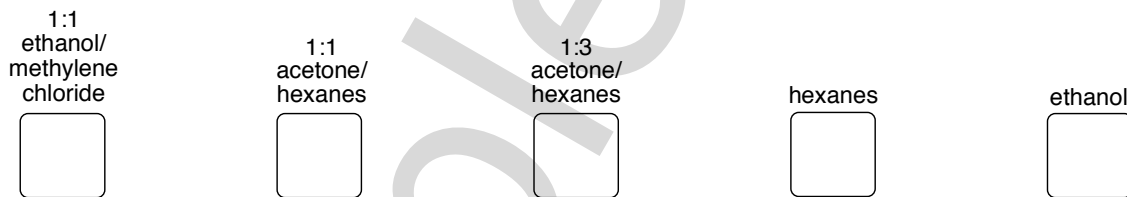
    A.  (3 pts) Rank the molecules in order of increasing retention time if they were eluted through a silica gel ($SiO_2$) stationary phase in a chromatography column with a 1:1 mixture of ethyl acetate and hexanes (1 = highest retention time; 4 = lowest retention time).
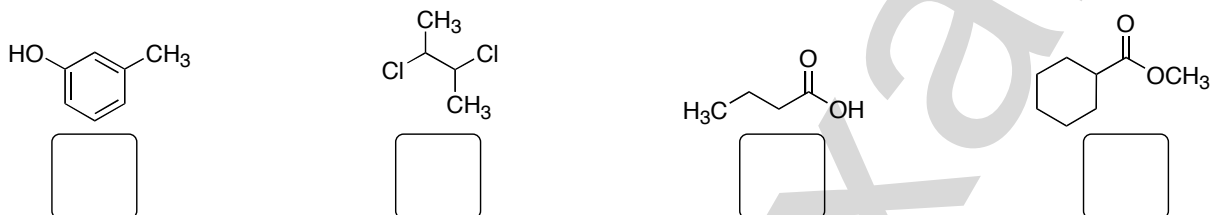
    B.  (3 pts) Rank the molecules in order of increasing equilibrium vapor pressure (1 = lowest $P^o$; 5 = highest $P^o$).
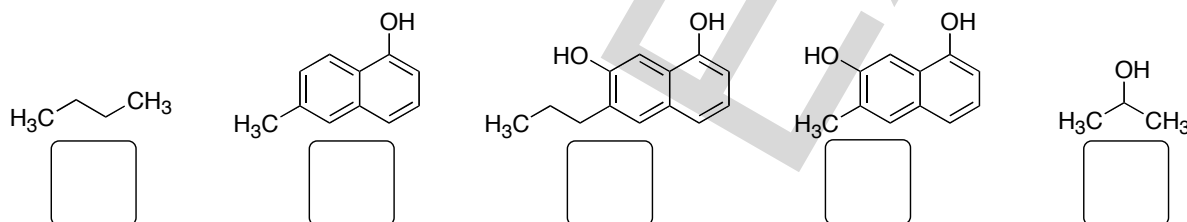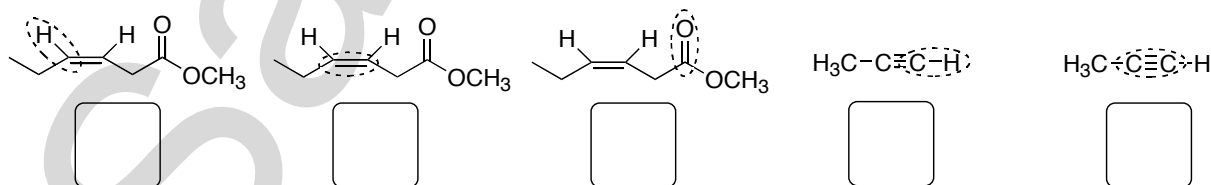
    C.  (3 pts) Rank each solvent in order of increasing polarity.  (1 = least polar; 5 = most polar).

    1:1 ethanol/ methylene chloride

    1:1 acetone/ hexanes

    1:3 acetone/ hexanes

    hexanes

    ethanol

    D.  (3 pts) Rank the molecules in order of increasing boiling point (1 = lowest boiling point; 4 = highest boiling point).
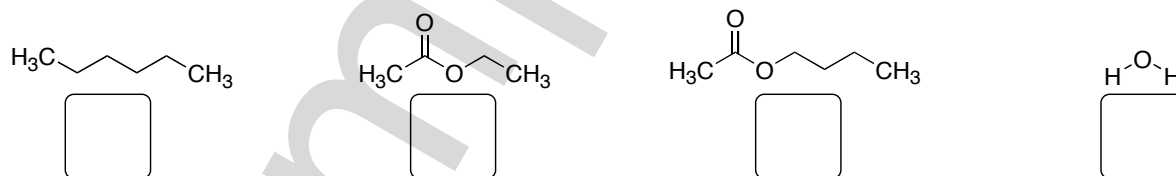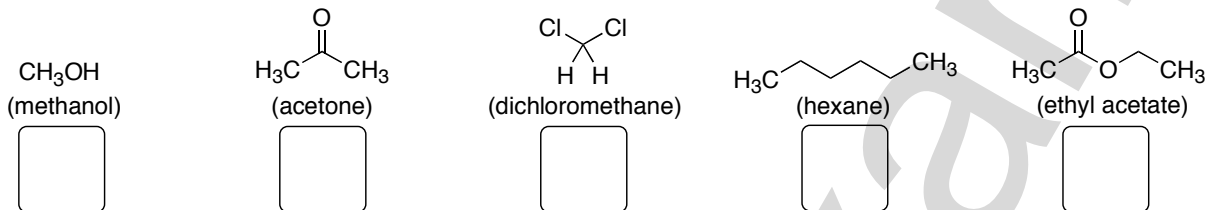
    E.  (3 pts) Rank each circled bond in order of increasing wavenumber ("frequency") in infrared spectroscopy (1 = lowest wavenumber; 5 = highest wavenumber).

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

F.  (3 pts) Rank each solvent in order of increasing eluting power in normal phase chromatography with a polar stationary phase (1 = lowest eluting power; 5 = highest eluting power).

CH$_3$OH
(methanol)

H$_3$C—C(O)—CH$_3$
(acetone)

Cl—CH$_2$—Cl
(dichloromethane)

H$_3$C~~~CH$_3$
(hexane)

H$_3$C—C(O)—O—CH$_3$ (ethyl acetate)
(ethyl acetate)

G.  (3 pts) Rank each pigment in order of increasing retention time on a gas-chromatograph column with a polar liquid stationary phase (1 = smallest retention time; 4 = larget retention time). *Hint: use what you know about theses pigment's TLC Rf-values to deduce their retention times.*
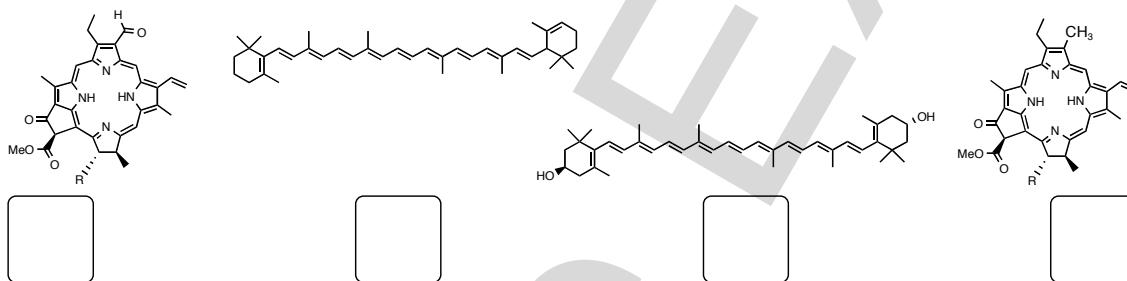
H.  (3 pts) Rank the molecules in order of increasing retention factor on a TLC plate with a polar stationary phase, such as silica gel (SiO$_2$) (1 = smallest retention factor; 4 = largest retention factor).
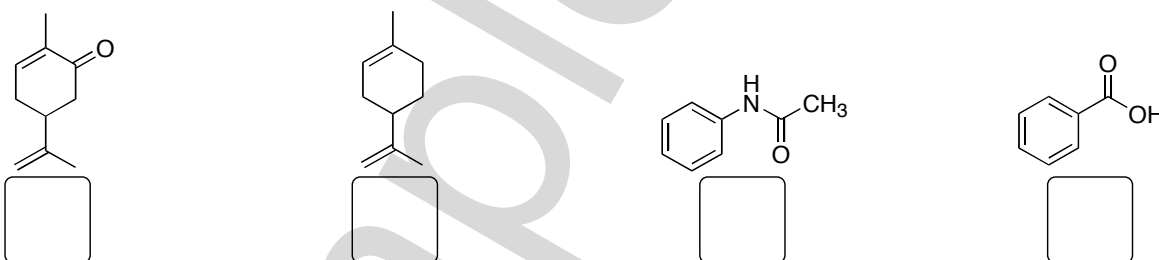
I.  (3 pts) Rank the pairs of atoms in order of increasing reduced mass (1 = smallest reduced mass; 5 = largest reduced mass).

$^{12}$C—$^{12}$C

$^{12}$C—$^{13}$C

$^{12}$C—D

$^{16}$O—D

$^{18}$O—H
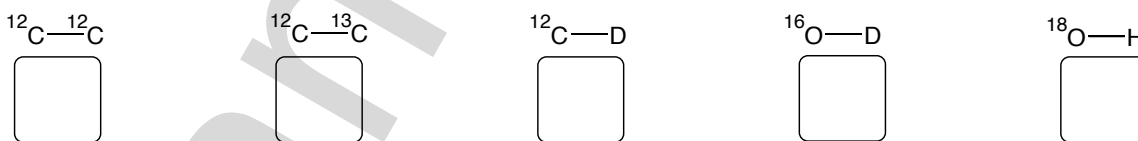
J.  (3 pts) Rank the bold hydrogen atoms in each molecule in order of increasing acidity (1 = least acidic, lowest pKa; 4 = most acidic). *Hint: the stronger the acid, the weaker the conjugate base and vice versa.*

Ph—C(O)—O**H**

**H**—CH$_3$

**H**—O—H

Ph—N(**H**)—C(O)—CH$_3$

Total Page Points: _____ of _____

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

2.  (10 pts) Consider the experimental description below for the separation of a mixture of benzoic acid and acetanilide by base extraction. The experimental methods and analyses contain a number of mistakes and oversights. Based upon your experience in the laboratory, find 10 of these errors and briefly state the nature of the error as well as a suitable correction. *No explanation & correction = no credit. List corrections below; do not make corrections within the paragraph itself.*

*A 1:1 mixture of benzoic acid and acetanilide was dissolved in diethyl ether and poured into a graduated cylinder. A 3.0 M basic aqueous solution of $Na_2CO_3$ was then added to the organic solution. Deprotonation of benzoic acid gives its conjugate base, benzamide, which is equally soluble in the aqueous phase and the organic phase. The two phases were then separated. The denser organic phase was the top layer. After separating the two phases, the organic phase was extracted with an additional portion of aqueous base. Likewise, the aqueous phase was extracted with an additional portion of organic solvent. Fewer extractions with larger volumes of extracting solvent result in more efficient extraction. The aqueous solution was neutralized with 3.0 M HCl, whereupon benzoic acid precipitated from solution and was collected by vacuum filtration on a Büchi funnel. Similarly, acetanilide was isolated by neutralizing the organic layer with 3.0 M HCl. Both solids were purified by recrystallization from boiling ethanol. The identity of each solid was confirmed by infrared spectroscopy. Both spectra exhibited an intense, sharp band at approximately 1200 $cm^{-1}$, which corresponds to the carbonyl functional group present in both. The purity of each solid was confirmed by melting point analysis since the melting points of pure substances are generally sharp (narrow melting range); impurities or mixtures generally cause melting point elevation and a broadening of the melting range.*

| Mistake/Error | Explanation & Correction |
|---|---|
| 1. | |
| 2. | |
| 3. | |
| 4. | |
| 5. | |
| 6. | |
| 7. | |
| 8. | |
| 9. | |
| 10. | |

3.  (4 pts) Using Hooke's law, calculate the frequency of the vibration in wavenumbers ($cm^{-1}$) for a carbonyl stretch where the isotopes of each atom in this functional group are $^{12}C$ and $^{18}O$. Show all work. *Hint: c = 3.0 x $10^{10}$ cm/s and k = 5 x $10^5$ dyne/cm for single bonds.*

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

4.  Morphine (**1**) is an opioid analgesic (pain killer) isolated from the opium poppy.  It is easily converted to derivatives, such as codeine (**2**), oxycodone (**3**) and heroin (**4**) through simple functional group transformations.
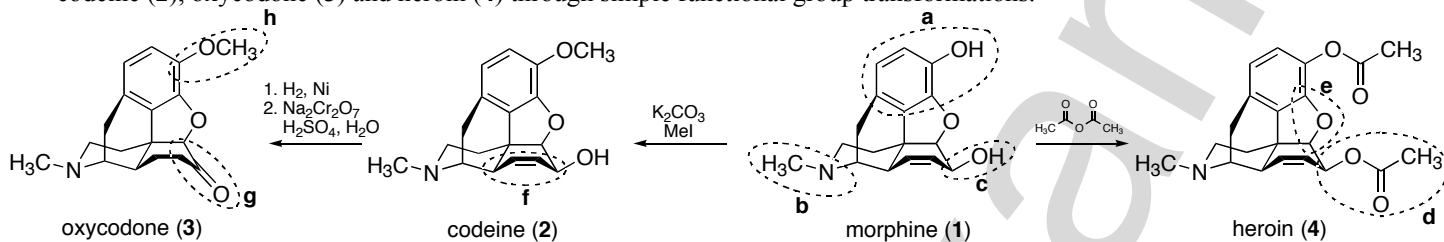


A.  (8 pts) Write the names of the functional groups circled in each opioid above.  Be as specific as possible.  For example, write *carboxylic acid*, not *carbonyl*.  The minimum atoms required to define each functional group are circled.

**a** _____     **e** _____

**b** _____     **f** _____

**c** _____     **g** _____

**d** _____     **h** _____

B.  (4 pts) The IR spectrum below was taken of a white powder suspected to be one of the opioids above.  Identify the opioid by writing the name in the space indicated.  Explain your decision by listing three pieces of reasoning in the box provided.  You may describe both the absence and presence of functional groups in the IR spectrum.  *Disambiguation: the C=C bonds of the benzene ring in all the opioids above occur at 1500 cm$^{-1}$ and 1450 cm$^{-1}$, which should not overlap with other C=C bonds.*
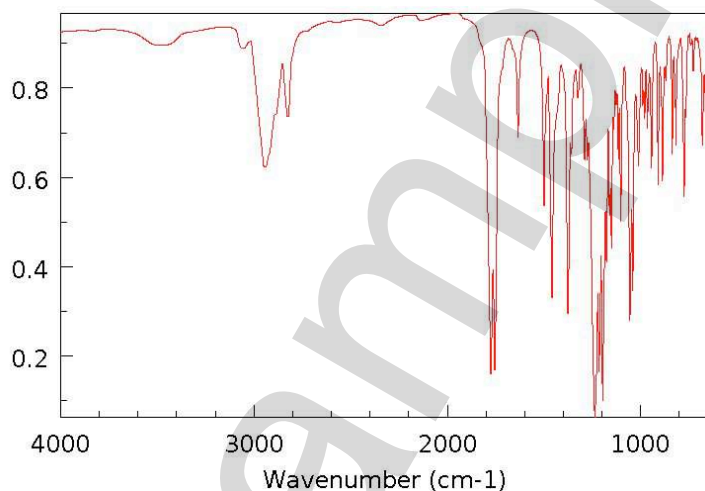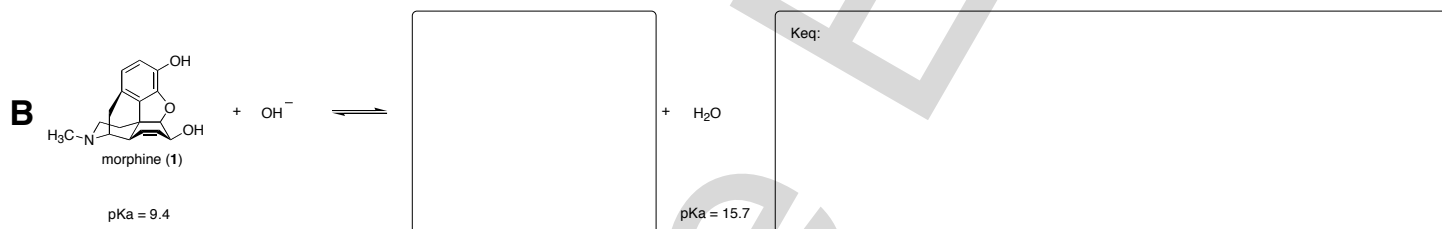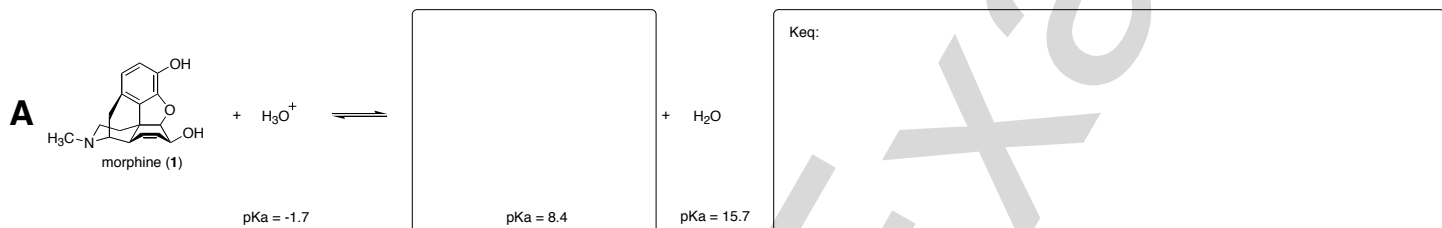


Opioid Name:

IR Analysis:

C.  (2 pts) Determine the index of hydrogen deficiency for heroin.  Show all work for credit.  *Hint: you do not necessarily have to determine the molecular formula to determine IHD; although that method will work as well.  If you do not use the molecular formula method, state how you determined IHD for full credit.*

Total Page Points: _____ of _____

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

D. Morphine is an amphoteric molecule since it contains both acidic and basic functional groups.
   a. (2 pts) In Equation A, the most basic functional group is protonated in aqueous acid. Draw the conjugate acid of morphine when this group when it is protonated in aqueous acid ($H_3O^+$). The pKa of the protonated group is 8.4.
   b. (2 pts) In Equation B, the most acidic functional group, which has a pKa of 9.4, is deprotonated in aqueous base. Draw the conjugate base of morphine when this group is deprotonated in aqueous base ($OH^-$).
   c. (2 pts) Determine whether morphine is more readily extracted by aqueous acid or aqueous base by determining the Keq for each equilibrium below. Show all work.

**A** 

morphine (**1**)

pKa = -1.7    +    $H_3O^+$    ⇌    [    ] pKa = 8.4    +    $H_2O$ pKa = 15.7

Keq:

**B**

morphine (**1**)

pKa = 9.4    +    $OH^-$    ⇌    [    ]    +    $H_2O$ pKa = 15.7

Keq:

5. (6 pts) Morphine is fairly soluble in water at a pH of 7.40 (physiological pH) since greater than 90% exists as the ammonium ion. Using the equation below, determine the minimum number of extractions with 10-mL portions of octanol that would be required to remove 95.0% of the morphine from 100 mL of water. The ocatnol:water partition coefficent is 1.42. Show all work. [*Hint:* $log_b(m)^n = n*log_b(m)$]

$$F_A = \left( \frac{V_o}{K V_x + V_o} \right)^n$$

6. (6 pts) Convert the following wavelengths and frequencies of electromagnetic energy into wavenumbers ($cm^{-1}$). Show all work. *Hint:* $c = 3.0 \times 10^{10}$ cm/s.

   a. 4.5 microns (μm)

   b. $5.7 \times 10^{-4}$ cm

   c. $9.0 \times 10^{13}$ Hz

Total Page Points: _____ of _____

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

7.  (8 pts) A Friedel-Crafts acylation of anisole (**5**) (1.62 g, 15 mmol) with acetyl chloride (**6**) (1.18 g, 15 mmol) affords a binary product with a total mass of 1.91 grams.  The product is analyzed by GLC equipped with a thermal conductivity detector.  The chromatogram shows two product peaks identified as *ortho*-methoxy acetophenone (**7**) (area = 12 mm$^2$; $W_f$ = 1.08; MW = 150.17 g/mol) and *para*-methoxy acetophenone (**8**) (area = 134 mm$^2$; $W_f$ = 1.02; MW = 150.17 g/mol).  Calculate the percent yield of each of the two isomeric products obtained in this reaction.  Show all work.

anisole (**5**):
M.W.: 108.14
1.62 g
15.0 mmol

acetyl chloride (**6**):
M.W.: 78.50
1.18 g
15.0 mmol

AlCl$_3$, THF
0 °C to rt, 4 h

*ortho*-methoxy acetophenone (**7**):
MW: 150.17 g/mol
GC area: 12 mm$^2$
$W_f$ = 1.08

*para*-methoxy acetophenone (**8**):
MW: 150.17 g/mol
GC area: 134 mm$^2$
$W_f$ = 1.02
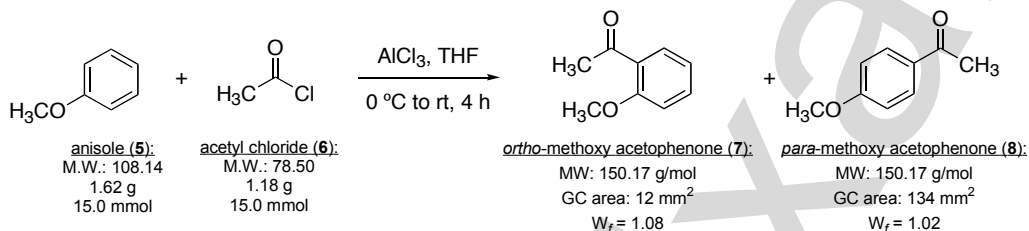
8.  (2 pts) List two modifications that could be made to the GLC experiment and/or equipment above to increase the retention times of <u>both</u> products.

9.  (2 pts) List two circumstances where a sharp melting point would be observed.

10. (2 pts) List two requirements for a recrystallization solvent.

Total Page Points: _____ of _____

Name_____(-1 pt)   TA Name_____(-1 pt)   UIN_____(-1 pt)

11. (10 pts) Match the infrared spectra below to their respective molecules by placing the numbers for each structure in the boxes next to each spectra. Each number is only used once.