THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FALL 2014
MIDTERM EXAMINATION

Chemistry 321

Name: _____ANSWER KEY_____

out of 25
~~28~~ **points total**

Date: Oct 23, 2014 **Time: 3:30-4:45 pm**

This exam contains **8** pages including the cover page.

Please count the pages and let me know immediately if you are missing a page.

This is a **closed book** examination. The use of **non-programmable** calculators is permitted.

For numerical questions, place your final answers in the boxes with the correct number of significant figures and units. **SHOW YOUR WORK** for full credit.

Avogadro's number $N_A = 6.0221367\times10^{23}$ molecules mol^{-1}

Molar gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.08205\ L\ atm\ mol^{-1}\ K^{-1}$

Planck constant $h = 6.6260755\times10^{-34}\ J\ s$

Speed of light $c = 2.99792458 \times 10^{8}\ m\ s^{-1}$

$1\ atm = 760\ torr = 1.0\times10^{5}\ Pa$

ideal gas law $PV=nRT$

Good luck!

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-0.5 (each incident, once per page) for sig figs more than 1 digit too many / too few

Avogadro's number $N_A = 6.0221367\times10^{23}$ molecules mol^{-1}

Molar gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1} = 0.08205\ L\ atm\ mol^{-1}\ K^{-1}$

Planck constant $h = 6.6260755\times10^{-34}\ J\ s$

Speed of light $c = 2.99792458\times10^{8}\ m\ s^{-1}$

1 atm = 760 torr = 1.0×10^{5} Pa

ideal gas law PV=nRT

Beer's law $I/I_0 = e^{-\eta\sigma L}$

ID: _____

Page	2	3	4	5	6	7	8	Total
out of	3.0	6.0	4.0	4.0	5.0	3.0	3.0	28.0
Score								

3 pts **1.** Hydrogen sulfide, H_2S, is destroyed in the troposphere by reaction with OH or Cl:

$H_2S + OH \rightarrow HS + H_2O$ $\quad k_{OH} = 6.1\times10^{-12}\, e^{(-75/T)}$ cm^3 molecule^{-1} s^{-1}

$H_2S + Cl \rightarrow HS + HCl$ $\quad k_{Cl} = 3.7\times10^{-11}\times e^{(210/T)}$ cm^3 molecules^{-1} s^{-1}

Assuming that the average abundance of OH in the troposphere equals 2.0×10^6 molecules cm^{-3}, that the average abundance of Cl in the troposphere equals 5.0×10^4 molecules cm^{-3}, and that the average temperature is 291 K, calculate the lifetime of H_2S in the troposphere (in units of days) with respect to oxidation by OH, by Cl, and by both.

$L(H_2S) = (k_{OH}[OH]+k_{Cl}[Cl])\times[H_2S] = 1/\tau_{total} \times [H_2S]$
or $(k_{OH}[OH]+k_{Cl}[Cl]) = 1/\tau_{total}$ **0.5 pts**

$= (6.1\times10^{-12}\, e^{(-75/291)}\times2.0\times10^6\ s^{-1} + 3.7\times10^{-11}\times e^{(210/291)}\times5.0\times10^4\ s^{-1}) \times [H_2S]$

$= (4.7\times10^{-12}\times2.0\times10^6\ s^{-1}+7.6\times10^{-11}\times5.0\times10^4\ s^{-1}) \times [H_2S]$

$= (9.4\times10^{-6}\ s^{-1}+3.8\times10^{-6}\ s^{-1}) \times [H_2S]$ **0.5 pts (both numbers correct)**

$= (1.3_2\times10^{-5}\ s^{-1}) \times [H_2S]$ **0.5 pts (numbers correct)**

$\Rightarrow \tau = 7.5_7\times10^4$ s $\times$ (1 day / 86400 s) = 0.88 days

$\tau_{OH} = (9.6\times10^{-6}\ s^{-1})^{-1} = 1.1\times10^5$ s
$\times$ (1 day / 86400 s) = 1.2 days

$\tau_{Cl} = (3.8\times10^{-6}\ s^{-1})^{-1} = 2.6\times10^5$ s
$\times$ (1 day / 86400 s) = 3.0 days

-0.5 pts if seconds not converted to days

Lifetime w.r.t. oxidation by OH (with units)	Lifetime w.r.t. oxidation by Cl (with units)	Lifetime w.r.t. oxidation by OH and Cl (with units)
1.2 days (**0.5 pts**)	3.0 days (**0.5 pts**)	0.88 days (**0.5 pts**)

average 88.4%

Good luck!

ID: _____

Page	2	3	4	5	6	7	8	Total
out of	3.0	6.0	4.0	4.0	5.0	3.0	3.0	28.0
Score								

3 pts **1.** Ethane, C_2H_6, is destroyed in the troposphere by reaction with OH or Cl:

$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$ $\quad k_{OH} = 7.7\times10^{-12}\, e^{(-1020/T)}$ cm^3 molecule^{-1} s^{-1}

$C_2H_6 + Cl \rightarrow C_2H_5 + HCl$ $\quad k_{Cl} = 7.2\times10^{-11}\times e^{(-70/T)}$ cm^3 molecules^{-1} s^{-1}

Assuming that the average abundance of OH in the troposphere equals 2.0×10^6 molecules cm^{-3}, that the average abundance of Cl in the troposphere equals 5.0×10^4 molecules cm^{-3}, and that the average temperature is 291 K, calculate the lifetime of C_2H_6 in the troposphere (in units of days) with respect to oxidation by OH, by Cl, and by both.

$L(C_2H_6) = (k_{OH}[OH]+k_{Cl}[Cl])\times[C_2H_6] = 1/\tau_{total} \times [C_2H_6]$
or $(k_{OH}[OH]+k_{Cl}[Cl]) = 1/\tau_{total}$ **0.5 pts**

$= (7.7\times10^{-12}\, e^{(-1020/291)}\times2.0\times10^6\ s^{-1} + 7.2\times10^{-11}\times e^{(-70/291)} \times 5.0\times10^4\ s^{-1}) \times [C_2H_6]$

$= (2.3\times10^{-12} \times 2.0\times10^6\ s^{-1}+5.7\times10^{-11} \times 5.0\times10^4\ s^{-1}) \times [C_2H_6]$

$= (4.6\times10^{-7}\ s^{-1}+2.8\times10^{-6}\ s^{-1}) \times [C_2H_6]$ **0.5 pts (both numbers correct)**

$= (3.2_9\times10^{-6}\ s^{-1}) \times [C_2H_6]$ **0.5 pts (numbers correct)**

$\Rightarrow \tau_{total} = 3.0_4\times10^5$ s $\times$ (1 day / 86400 s) = 3.5 days

$\tau_{OH} = (4.6\times10^{-7}\ s^{-1})^{-1} = (2.2\times10^6$ s) $\times$ (1 day / 86400 s) = 25 days

$\tau_{Cl} = (2.8\times10^{-6}\ s^{-1})^{-1} = (3.5\times10^5$ s) $\times$ (1 day / 86400 s) = 4.1 days

-0.5 pts if seconds not converted to days

Lifetime w.r.t. oxidation by OH (with units)	Lifetime w.r.t. oxidation by Cl (with units)	Lifetime w.r.t. oxidation by OH and Cl (with units)
25 days **0.5 pts**	4.1 days **0.5 pts**	3.5 days **0.5 pts**

85.2%

6 pts **2.** Define the following terms:

a. Eutrophication

the increase of mineral and organic nutrients in a body of water such that the dissolved oxygen is reduced to favor plant over animal life.

0.25/1 if only "run-off of fertilizer" or "nutrients accumulate in ocean" and no explanation

-0.25 if only mention 1 nutrient (e.g., nitrogen)

---

b. Respirable particle

Aerosol particle that belongs to $PM_{2.5}$ (<2.5 μm in size). When inhaled, it enters deep into the lung

0.25/1 if explanation correct but respirable and inhalable confused

0.25/1 if 2.5 nm instead of 2.5 μm

---

c. Nitrogen fixation

Conversion of gaseous N_2 to "fixed forms" (i.e., NO_3^-, NO_2^-, and/or NH_4^+), usually by bacteria

-0.25 if charges missing on species

-0.25 if the word "condensed" is used

-0.5 if not a surface process

---

d. Odd oxygen

$O_x = O + O_3$

---

e. Global biogeochemical element cycle

dynamic circulation of elements between the Atmosphere, Hydrosphere, Geosphere, Biosphere, and – since human activities emit chemical elements – the Anthrosphere.

-0.25 if "substance" or "molecules" or "chemical species" instead of element

-0.5 if spheres not listed

-0.5 if aerosol are referred to as substances or molecules

---

f. Greenhouse effect

greenhouse gases "absorb" outgoing radiation (from the Earth's surface) in the thermal IR, and hence and trap heat near the surface

- 0.5 if outgoing IR not mentioned
- 0.25 if not recognizing outgoing IR as thermal (e.g., by calling it "reflected" IR)
- 0.5 if the word "scattering" is used instead of absorption; - 0.25 if both are used
- 0.25 "radiation" without mentioning IR or infrared

1

×4

79.6%

6 pts **2.** Define the following terms:

a. Global biogeochemical element cycle

dynamic circulation of elements between the Atmosphere, Hydrosphere, Geosphere, Biosphere, and – since human activities emit chemical elements – the Anthrosphere.
-0.25 if "substance" or "molecules" or "chemical species" instead of element
-0.5 if spheres not listed

---

b. Nitrification

oxidation of NH_4^+ (or NH_3) to NO_3^- and NO_2-
$NH_4^+ \rightarrow NO_3^- \rightarrow NO_2^-$
-0.25 if charges missing on species

---

c. Reservoir species

A species that by itself is not chemically active, but can release a chemically active species. Example: $ClNO_3$, which can release Cl and NO_x.
0.25/1 if only stated that res. species are unreactive w/o giving example
-0.5 if notion that reservoir species release active species not conveyed

---

d. Tropopause

Region of the atmosphere between troposphere and stratosphere; marked by a temperature inversion (lower temp than in troposphere below and stratosphere above)

---

e. Inhalable particle

Aerosol particle that belongs to PM_{10} (<10 μm in size). When inhaled, it does NOT enter deep into the lung.
0.25 pt if explanation correct but respirable and inhalable confused.
Note: PM_{10} includes $PM_{2.5}$, so it's not incorrect to associate PM_{10} with health effects, even though most PM_{10} is not associated with health effects; most inhalable particles are NOT associated with health effects
-0.5 if aerosol are referred to as substances or molecules

---

f. null cycle

A series or sequence of reactions whose overall reaction does not contain a chemical change (i.e., produce or remove a species).
-0.5 if multiple reactions not identified
-0.25 if the term "cycle" not defined

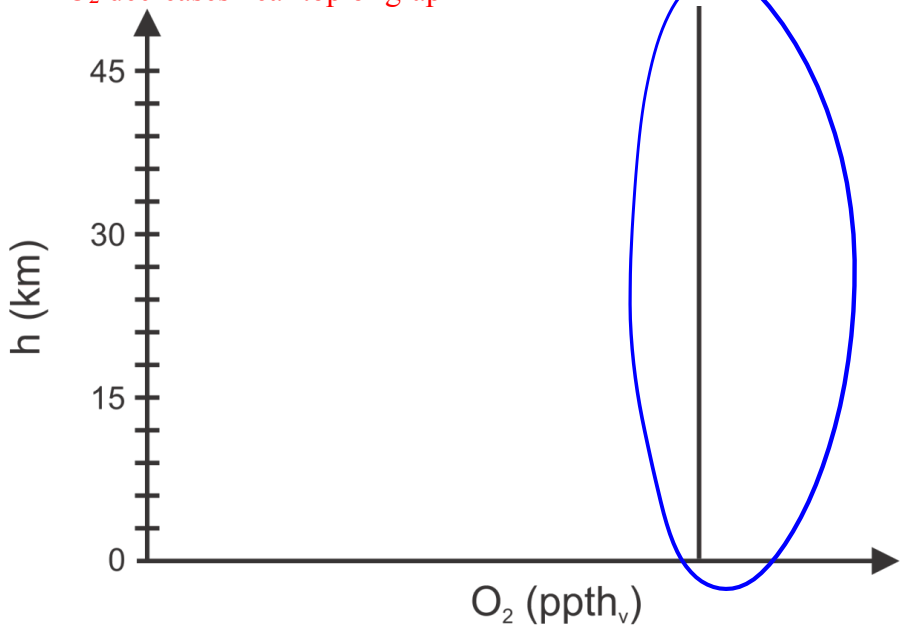
77.2 %

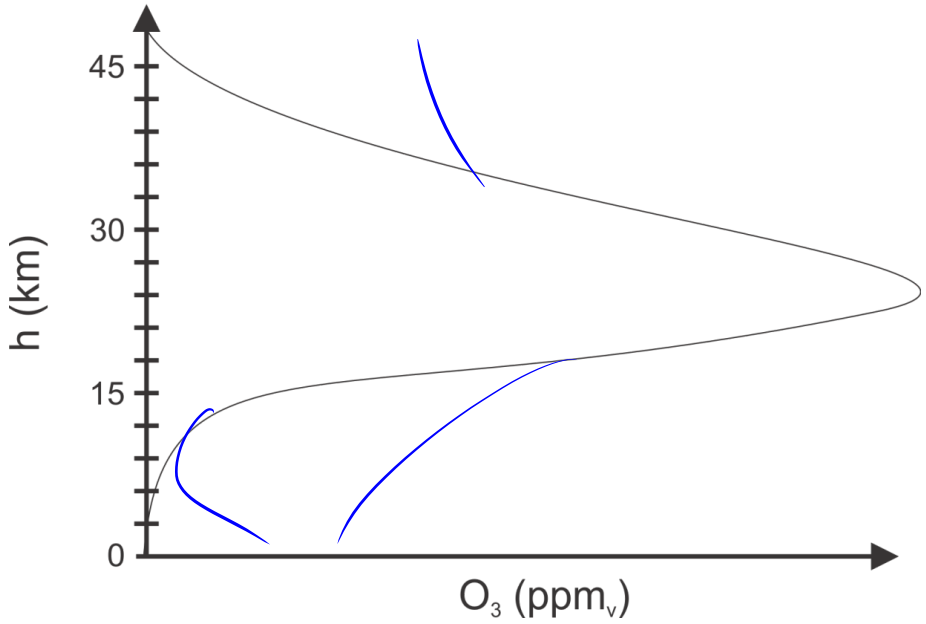
4 pts **3.** Sketch the approximate atmospheric profile of oxygen and ozone (height above ground from 0 to 50 km plotted against mixing ratio) that is predicted by the Chapman mechanism.

-1 if ozone increases near surface or if ozone mixing ratios at surface similar or stratospheric levels

- 0.5 if "tropopause" written next to the max. O_3 mixing ratio.

-1 if O_2 decreases near top of graph





55.4 %

4 pts **3.** Sketch the approximate atmospheric oxygen and ozone profile (height above ground from 0 to 50 km plotted against mixing ratio) that is predicted by the Chapman mechanism.

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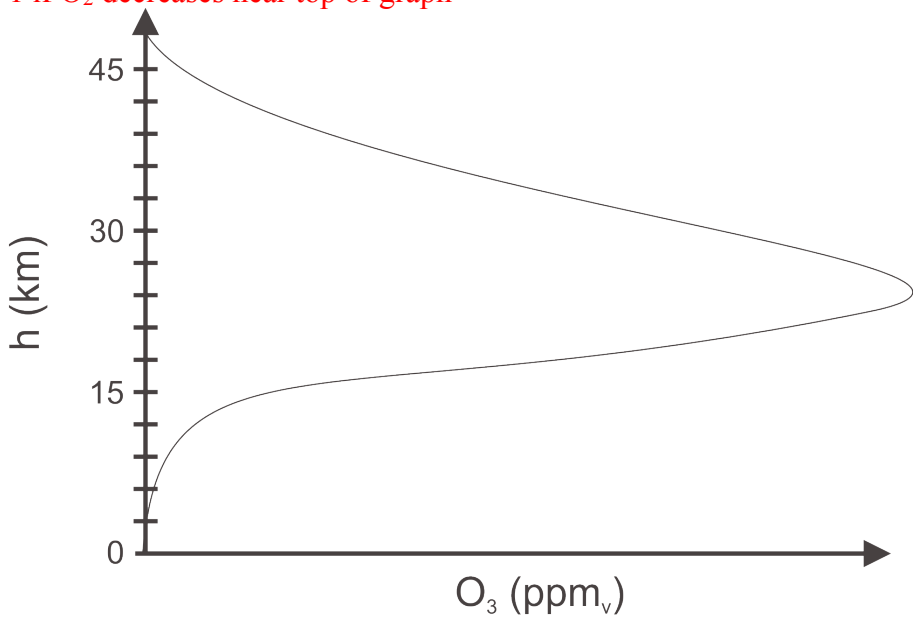
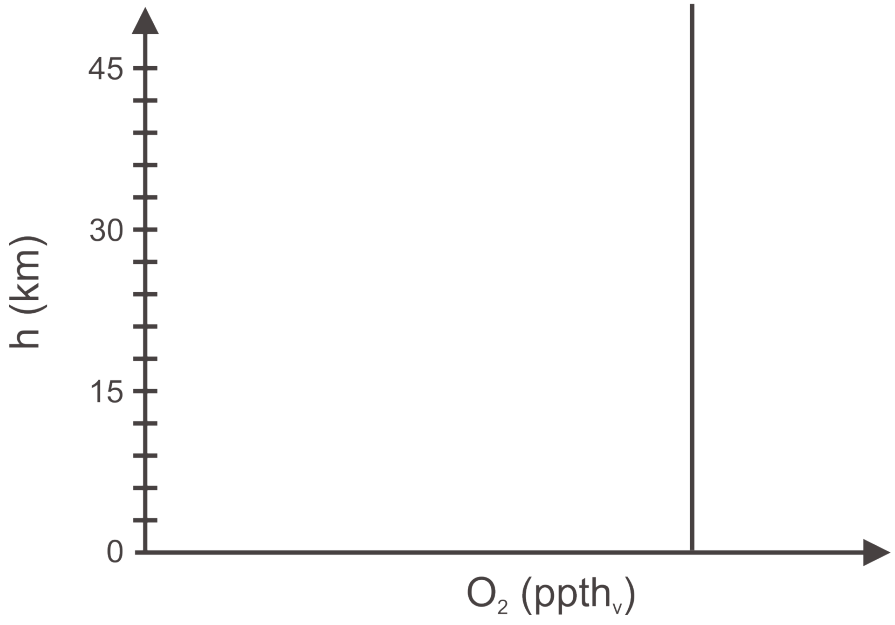




61.8%

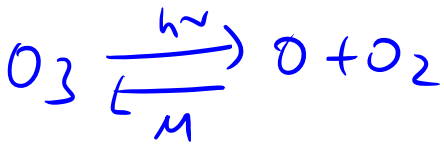
2 pts **4.** What is the difference between a 2-way and a 3-way catalytic converter?

A 3-way catalytic converter reduces NO_x to N_2 and completely oxidizes CO and partially oxidized hydrocarbons to CO_2 and H_2O using Pt-Rh catalyst

A 2-way catalytic converter only completes the oxidation of CO and partially oxidized hydrocarbons to CO_2 and H_2O (usually only Pt catalyst).

(2 points if difference stated correctly)
0.5/2 if only stating that there is a different (more efficient) catalyst
0.5/2 if types of reactions stated but wrong difference identified

2 pts **5.** Explain why ozone, which photo-dissociates at wavelengths of <1184 nm, does not vanish in the troposphere during the day.
Note: this question was on assignment #2.



Short answer: odd oxygen is conserved.

O_3 photo-dissociates to O and O_2. The main fate of O is reaction with O_2 to reform O_3. So its not removed quickly, even though its lifetime (with respect to photo-dissociation) is short. In other words, what controls a rate of change of a compound is both production and loss terms, i.e., is $d/dt[O_3] = P - L$, and $L >> L-P$.

Some O_3 is replenished by transport of O_3 from the stratosphere, but this is a rather small term. (**0.5 pt if only this is argued)**
There is also NO_x/HO_x catalyzed ozone production, which requires VOCs to be oxidized. Again, a rather small term for most of the troposphere (exception: polluted cities). (**0.5 pt if only this is argued)**

- 1 pt if $O_2+h\nu$ is mentioned as a possibility in the troposphere

49.2 %

2 pts **4.** Explain why ozone, which photo-dissociates at wavelengths of <1184 nm, does not vanish in the troposphere during the day.
Note: this question was on assignment #2.

Short answer: odd oxygen is conserved.

O_3 photo-dissociates to O and O_2. The main fate of O is reaction with O_2 to reform O_3. So its not removed quickly, even though its lifetime (with respect to photo-dissociation) is short. In other words, what controls a rate of change of a compound is both production and loss terms, i.e., is $d/dt[O_3] = P - L$, and $L >> L-P$.

Some O_3 is replenished by transport of O_3 from the stratosphere, but this is a rather small term. (**0.5 pt if only this is argued)**
There is also NO_x/HO_x catalyzed ozone production, which requires VOCs to be oxidized. Again, a rather small term for most of the troposphere (exception: polluted cities). (**0.5 pt if only this is argued)**

- 1 pt if $O_2+h\nu$ is mentioned as a possibility in the troposphere

2 pts **5.** What is the difference between a 2-way and a 3-way catalytic converter?

A 3-way catalytic converter reduces NO_x to N_2 and completely oxidizes CO and partially oxidized hydrocarbons to CO_2 and H_2O using Pt-Rh catalyst

A 2-way catalytic converter only completes the oxidation of CO and partially oxidized hydrocarbons to CO_2 and H_2O (usually only Pt catalyst).

(2 points if difference stated correctly)
0.5/2 if only stating that there is a different (more efficient) catalyst
0.5/2 if types of reactions stated but wrong difference identified

48.2%

5 pts **6.** Explain why stratospheric ozone depletion occurs over the South Pole. Give relevant chemical reactions.

During winter and darkness, the arctic Vortex forms 0.5 pt
isolating the south pole; 0.5 pt
which gets very cold 0.5 pt
(because of the low heat capacity of Antarctica compared to the Arctic ocean) 0.5 pt
creating conditions favoring formation of the polar stratospheric clouds 0.5 pt
which are formed from water and nitric acid (nitric acid trihydrate) 0.5 pt
The PSCs catalyze the reaction $ClNO_3 + HCl \rightarrow Cl_2 + HNO_3$ 0.5 pt
After arctic sunrise, chlorine photodissociates $Cl_2 + h\nu \rightarrow 2Cl$ 0.5 pt
The usual termination step, $ClO+NO_2 \rightarrow ClNO_3$ is not efficient as the PSCs activate
this reservoir species via the reactions above 0.5 pt
This Cl source adds to the "usual" Cl source, CFC photolysis:
$CFC + h\nu \rightarrow Cl + products$ 0.5 pt
Cl atoms catalytically destroy ozone 0.5 pt
via $Cl + O_3 \rightarrow ClO + O_2$ 0.5 pt
and $ClO + O \rightarrow Cl + O_2$ 0.5 pt

up to 6.5 points possible - max 5 points

IMPORTANT: Some of you incorrectly wrote Cl^- (with a "dash") when trying to refer to the radical (Cl•, with a "dot"). The minus sign (dash) implies a negative charge; for chlorine, this means a complete valence shell (8 electrons), which is NOT a radical as all electrons are paired. The radical species (Cl•), on the other hand, has 7 valence electrons; the odd number of electrons implies that one electron is unpaired, which is the definition of a "radical species".

54.9%

5 pts

6. Explain why stratospheric ozone depletion occurs over the South Pole. Give relevant chemical reactions.

During winter and darkness, the arctic Vortex forms 0.5 pt
isolating the south pole; 0.5 pt
which gets very cold 0.5 pt
(because of the low heat capacity of Antarctica compared to the Arctic ocean) 0.5 pt
creating conditions favoring formation of the polar stratospheric clouds 0.5 pt
which are formed from water and nitric acid (nitric acid trihydrate) 0.5 pt
The PSCs catalyze the reaction $ClNO_3 + HCl \rightarrow Cl_2 + HNO_3$ 0.5 pt
After arctic sunrise, chlorine photodissociates $Cl_2 + h\nu \rightarrow 2Cl$ 0.5 pt
The usual termination step, $ClO+NO_2 \rightarrow ClNO_3$ is not efficient as the PSCs activate
this reservoir species via the reactions above 0.5 pt
This Cl source adds to the "usual" Cl source, CFC photolysis:
CFC $+ h\nu \rightarrow$ Cl + products 0.5 pt
Cl atoms catalytically destroy ozone 0.5 pt
via $Cl + O_3 \rightarrow ClO + O_2$ 0.5 pt
and $ClO + O \rightarrow Cl + O_2$ 0.5 pt

up to 6.5 points possible - max 5 points

IMPORTANT: Some of you incorrectly wrote Cl^- (with a "dash") when trying to refer to the radical (Cl•, with a "dot"). The minus sign (dash) implies a negative charge; for chlorine, this means a complete valence shell (8 electrons), which is NOT a radical as all electrons are paired. The radical species (Cl•), on the other hand, has 7 valence electrons; the odd number of electrons implies that one electron is unpaired, which is the definition of a "radical species".

53.0 %

3 pts **7.** **7a**. Which of the following likely has the shortest lifetime in the troposphere?

A. CH_2Cl_2
B. CCl_4
C. $CBrCl_3$
D. CF_2Cl_2
E. SF_6
F. CF_4
G. All have the same lifetime.

7b Which are secondary aerosols?

A. Sea salt aerosol
B. Mineral Dust aerosol
C. Biomass burning aerosol (Wood smoke)
D. Ammonium sulfate aerosol **1/3**
E. Ammonium bisulfate aerosol **1/3**
F. Ammonium nitrate aerosol **1/3**
G. Bioaerosols (Pollen)
H. A, B and C
I. A, B, C, and G
J. D and F **2/3**
K. D, E, and F
L. A, D, and E
M. all the above
N. None of the above

7c. Consider NO and NO_2 in the troposphere. Which of the following statements is not true?

A. There is a photostationary steady state between NO oxidation and NO_2 photolysis.
B. The steady concentrations shift towards NO_2 as oxidant levels in the troposphere increase.
C. The steady state concentrations shift towards NO as the NO_2 photolysis frequency increases.
D. The ratio of NO to NO_2 is usually independent from the ratio at which both were emitted.
E. All of the above statements (A-D) are true.
F. All of the above statements (A-D) are false.

56.4%

3 pts **7a**. The greenhouse effect

A. arises from absorption of infrared radiation originating from the sun.
B. is primarily caused by SF_6.
C. has to date had a negligible effect on surface temperatures.
D. arises from scattering of infrared radiation emitted by the Earth's surface.
E. arises from absorption of infrared radiation emitted by the Earth's surface. 0.5
F. is caused by gases such as carbon dioxide, water, methane, nitrous oxide, ozone, and halocarbons. 0.5
G. E and F.
H. D, E, and F.
I. All of the above.
J. None of the above.

7b What acids are mainly responsible for acid rain?

A. Carbonic acid
B. Sulfuric acid 1/3
C. Sulfurous acid 1/3
D. Ascorbic acid
E. Nitric acid 1/3
F. A, B, and E
G. B, C, and E
H. B and C 2/3
I. D, C, and B
J. All of the above
K. None of the above

7c. Which of the following likely has the shortest lifetime in the troposphere?

A. CF_2Cl_2
B. $CBrCl_3$
C. CCl_4
D. CH_2Cl_2
E. SF_6
F. CF_4
G. All have the same lifetime.

51.0%

3 pts

7d. What acids are mainly responsible for acid rain?

A. Carbonic acid
B. Sulfuric acid **1/3**
C. Sulfurous acid **1/3**
D. Ascorbic acid
E. Nitric acid **1/3**
F. A, B, and E
G. B, C, and E
H. B and C **2/3**
I. D, C, and B
J. All of the above
K. None of the above

$CO_2 \rightleftharpoons CO_{2(g)}$
(aq)

7e. The greenhouse effect

A. arises from absorption of infrared radiation originating from the sun.
B. is primarily caused by SF_6.
C. has to date had a negligible effect on surface temperatures.
D. arises from scattering of infrared radiation emitted by the Earth's surface.
E. arises from absorption of infrared radiation emitted by the Earth's surface. **0.5**
F. is caused by gases such carbon dioxide, water, methane, nitrous oxide, ozone, and halocarbons. **0.5**
G. E and F.
H. D, E, and F.
I. All of the above.
J. None of the above.

7f. How many vibrational modes are there in isoprene (C_5H_8)?

A. 99
B. 77
C. 37
D. 36
E. 35
F. 34
G. 33
H. 32
I. 31
J. 30
K. 15
L. 9
M. 8
N 6.5
O 5
P 0
Q None of the above

$3N - 6$

$3 \times 13 - 6$

59.1%

3 pts **7d**. Consider NO and NO_2 in the troposphere. Which of the following statements is not true?

A. There is a photostationary steady state between NO oxidation and NO_2 photolysis.
B. The steady concentrations shift towards NO_2 as oxidant levels in the troposphere increase.
C. The steady state concentrations shift towards NO as the NO_2 photolysis frequency increases.
D. The ratio of NO to NO_2 is usually independent from the ratio at which both were emitted. Not at night and when $[NO_x] > [O_3]$
E. All of the above statements (A-D) are true.
F. All of the above statements (A-D) are false.

7e. Which are primary aerosols?

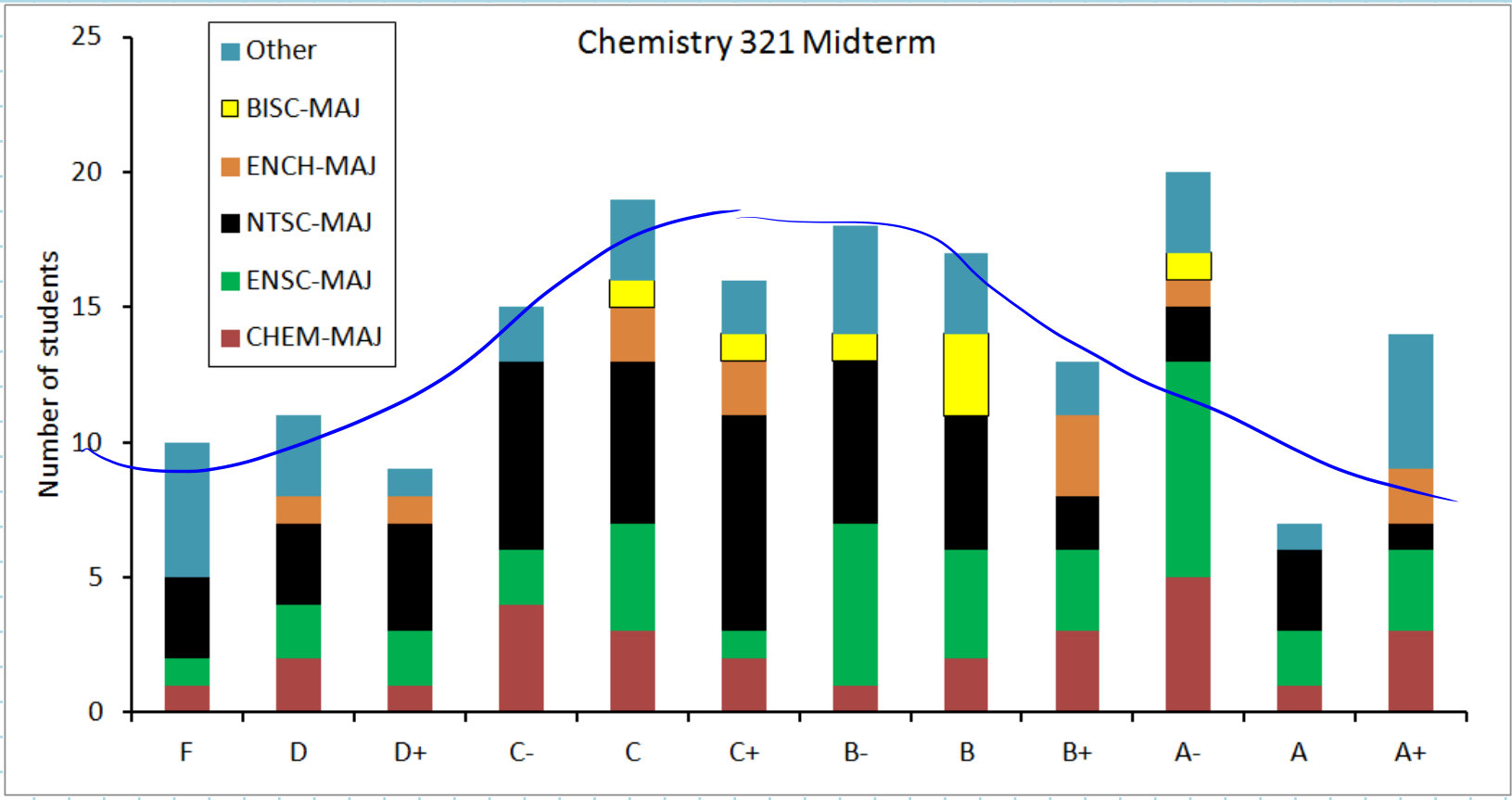
A. Sea salt aerosol 0.25
B. Mineral Dust aerosol 0.25
C. Biomass burning aerosol (Wood smoke) 0.25
D. Ammonium sulfate aerosol
E. Ammonium bisulfate aerosol
F. Ammonium nitrate aerosol
G. Bioaerosols (Pollen) 0.25
H. A, B and C 0.75
I. A, B, C, and G
J. D and F
K. D, E, and F
L. A, D, and E
M. all the above
N. None of the above

7f. How many vibrational modes are there in isopentane (C_5H_{12})?

A. 99
B. 77
C. 47
D. 46
E. 45
F. 44
G. 43
H. 42
I. 41
J. 40
K. 36
L. 15
M. 12
N. 8.5
O. 5
P. 0
Q. None of the above

62.7%

max = 28/28


Chemistry 321 Midterm
Other
BISC-MAJ
ENCH-MAJ
NTSC-MAJ
ENSC-MAJ
CHEM-MAJ
Number of students
25
20
15
10
5
0
F
D
D+
C-
C
C+
B-
B
B+
A-
A
A+