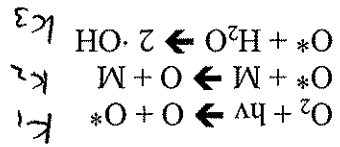


Chemistry & Biochemistry 123
 Environmental Chemistry
 Winter 2008
 Final Examination, In-class

NAME Answer Key
 PERM # _____

PROBLEM	POINTS/POSSIBLE
1	/15
2	10 15
3	10 15
4	/15
5	/15
6	/15
7	/15
8	/15
9	/40
TOTAL	/160

1. A. For the following 3-step mechanism for the production and destruction of excited oxygen atoms in the atmosphere, develop an expression for the steady-state concentration of O^* in terms of the concentrations of the other species involved.



$$\frac{d[O^*]}{dt} = 0 = k_1[O_2] - k_2[O^*][M] - k_3[O^*][H_2O]$$

$$-k_3[O^*][H_2O]$$

$$k_1[O_2] = k_2[O^*][M] + k_3[O^*][H_2O]$$

$$= [O^*][k_2[M] + k_3[H_2O]]$$

$$[O^*] = \frac{k_1[O_2]}{k_2[M] + k_3[H_2O]}$$

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1. B. Is the sequence of reactions listed above likely to occur in the lower troposphere? Explain why or why not. Give two reasons.

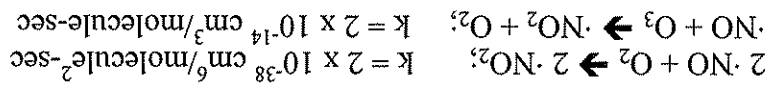
Not likely:

- i) inversely dependent on M , and $[M]$ is high
- ii) required hv energy is $< 242 \text{ nm}$, and these photons do not penetrate

(or two)

6

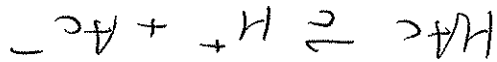
2. Consider a photochemical smog episode in which the concentration of ozone is 40 ppb and the concentration of $\cdot\text{NO}$ is 80 ppb. Under conditions of standard temperature and pressure ($T = 25^\circ\text{C}$, $P = 1\text{ atm}$), separately calculate the rates of $\cdot\text{NO}$ oxidation by O_2 and by O_3 , given the following information:



$R = 0.082 \text{ L-atm/mol}\cdot^\circ\text{K}$
 Partial pressure of $\text{O}_2 = 0.21 \text{ atm}$

See Sample Problem Set 3, ungraded,
Problem 10

3. Acetic acid dissociates in pure water with $K_a = 1.8 \times 10^{-5} M$, to an extent less than 5%. Given these data, calculate the pH of a 0.1 M solution of sodium acetate.



$$K_b = K_w / K_a = 5.56 \times 10^{-10} M$$

Since, from equations

$$[HAc] = [OH^-]$$

$$\rightarrow K_b = [OH^-]^2 / [Ac^-]$$

Because HAc is not appreciably dissociated

the $[Ac^-]$ is not significantly greater than 0.1M

$$\rightarrow [Ac^-] = 0.1 M$$

$$\rightarrow [OH^-]^2 = (5.56 \times 10^{-10}) (0.1)$$

$$\rightarrow [OH^-] = 7.46 \times 10^{-6} M$$

$$\rightarrow pOH = 5.13$$

$$pH = 14 - 5.13 = 8.87$$

4. What is the effect on the atmospheric CO₂ level caused by each of the following? Explain your answer in two or three sentences each.

(a) operation of the "biological pump" in the euphotic zone of a large lake

Effect is to lower [CO₂] significantly.
In the euphotic zone CO₂ is fixed by phytoplankton organisms, which provide food for other heterotrophs. Dead organisms fall below the euphotic zone in a carbon sink, called the biological pump which promotes greater CO₂ transfer rates from the atmosphere

(b) weathering of limestone rocks on land, followed by transfer of the dissolved calcium ions into the oceans

There is NO NET EFFECT here,

The weathering reaction consists of the uptake

of CO₂ from the atmosphere, but reaction with

limestone rocks result in dissolution of Ca⁺⁺

and HCO₃⁻, which go into the ocean,

Then, in the ocean, Ca⁺⁺ and HCO₃⁻ react

to form CaCO₃ which, in equilibrium w/CO₂

+H₂O, outgasses the CO₂ back to the

(c) on Mars, elimination of tectonic activity arising from cooling of the planetary core

Effect is to draw down the CO₂ concentration,

because tectonic activity, under conditions of

high temperature and pressure, reverses the

weathering reaction, liberating CO₂.

Over geologic time, this complets both

the organic and inorganic C cycles

on Earth.

5. Consider the following data:

Gas	Concentration	Residence Time	Global warming efficiency relative to CO ₂
CH ₄	1.77 ppm	12 years	23
N ₂ O	316 ppb	120 years	296
CHF ₂ Cl	0.15 ppb	12 years	1700

(a) What accounts for the capacity of these gases to provide much higher per-molecule warming effects as compared to CO₂?

CO₂ absorption peak in the IR, within the spectrum of Earth's IR emission, is in the 14,000 nm region, where much of the emitted IR has already been absorbed. Therefore the per-molecule effect of additional CO₂ is low. By contrast, CH₄, N₂O and CHF₂Cl all absorb IR in the "atmospheric window" at about 800-1000 nm, where existing gases absorb little IR. So their effects are relatively much greater.

(b) Which of these gases is presently input into the atmosphere at the highest rate? Show the calculation.

CH₄: $1.77 \text{ ppm} / 12 \text{ years} = 0.15 \text{ ppm/yr}$
 N₂O: $316 \text{ ppb} = 0.316 \text{ ppm} / 120 \text{ years} \sim 0.0026 \text{ ppm/yr}$
 CHF₂Cl: $0.00015 \text{ ppm} / 12 \text{ years} \sim 0.000125 \text{ ppm/yr}$
 → Methane is highest

(c) Which of these gases is presently making the largest contribution to global warming? Show how you calculate this given the data above.

Can be estimated from (input rate) × (efficiency)

CH₄: $0.15 \text{ ppm/yr} \times 23 = 3.45$

N₂O: $0.0026 \times 296 = 0.77$

CHF₂Cl: $0.000125 \times 1700 = 0.21$

Methane

6. (a) Consider a photochemical smog episode. Which of the following gases are primary pollutants? Which are secondary pollutants?

(5)

O₃, ROONO₂, ·OOH, ·NO, CH₂O, ·NO₂, HNO₃, C₂H₄, H₂SO₄, SO₂

0.5 each

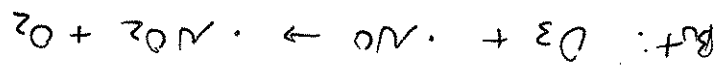
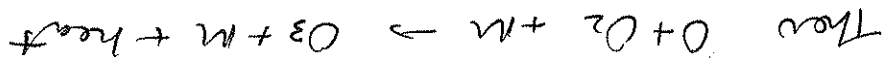
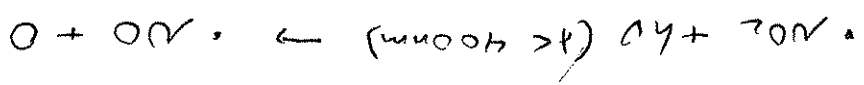
Primary pollutants: ·NO, C₂H₄, SO₂, (·NO₂)

Secondary pollutants: O₃, ROONO₂, ·OOH, H₂SO₄, CH₂O, HNO₃

(·NO₂)

(b) Why can't a photochemical smog episode proceed in the absence of hydrocarbons? Explain as thoroughly as you can. Be sure to identify the most crucial reaction, writing out the identity of the species involved.

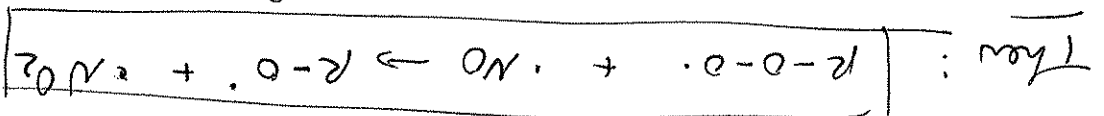
Required atomic O produced from ·NO₂:



so the O₃ is destroyed and cannot be

built up.

-hydrocarbons produce alkyl radicals by reaction w/ ·OH, and these form alkyl peroxy radicals (R-O-O·) after reaction w/ O₂



The ·NO is removed as an O₃ sink and more ·NO₂ is generated for further photo decomposition → more O

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7. What effect would doubling of the present-day CO_2 concentration have on the pH of rain that is

otherwise unpolluted?

$K_H = 0.032 \text{ M/atm}$; $K_a [\text{H}_2\text{CO}_3] = 4.0 \times 10^{-7}$. H_2CO_3 is less than 5% dissociated.

Based on the results of your calculation, comment on whether doubling atmospheric CO_2 would worsen the acid rain problem as it presently exists in polluted environments where the concentrations of SO_2 are significant.

Present day $[\text{CO}_2] \sim 350 \text{ ppm} = 350 \times 10^{-6} \text{ ATM}$

$$K_H = [\text{H}_2\text{CO}_3(\text{aq})] / P_{\text{CO}_2}$$

$$\rightarrow [\text{H}_2\text{CO}_3] = 1.22 \times 10^{-5} \text{ M}$$



$$[\text{H}^+] = [\text{HCO}_3^-]$$

$$[\text{H}_2\text{CO}_3] = 1.22 \times 10^{-5} \text{ M}$$

$$\rightarrow [\text{H}^+]^2 = K_a [\text{H}_2\text{CO}_3] \rightarrow \text{pH} = 5.656$$

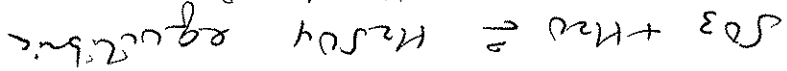
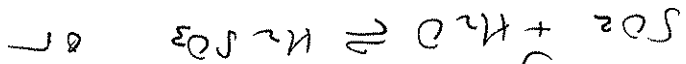
!f $[\text{CO}_2] = 760 \text{ ppm}$, using above equations

$$\rightarrow [\text{H}_2\text{CO}_3] = 2.43 \times 10^{-5} \text{ M}$$

$$\text{pH} = 5.501$$

\rightarrow The pH is decreased by only ~ 0.15 unit.

\rightarrow If $[\text{SO}_2]$ are significant, the pH of the acid rain will be controlled by the



either of these result in pH at least

one full unit lower, so the acid rain problem would not be worsened by doubled $[\text{CO}_2]$.

8. (a) The process by which nitrate anion is converted to N_2 gas is known as:

(i) nitrogen fixation

(ii) denitrification

(iii) nitrification

(iv) nitrate assimilation

(b) For the following reaction: $SO_4^{2-} + 2 CH_2O + 2 H^+ \rightleftharpoons H_2S + 2 H_2O + 2 CO_2$

the number of electrons transferred is:

(i) 0

(ii) 2

(iii) 4

(iv) 6

(v) 8

(c) Which statement is TRUE? The phenomenon of acid mine drainage:

(i) only occurs during aerobic conditions

(ii) produces insoluble iron in the +2 oxidation state

(iii) results in the reduction of sulfur

(iv) produces elemental sulfur, which is generally nontoxic

(d) Which of the following elements is likely to limit aquatic biological growth in an environment near to where agriculture is intensively practiced?

(i) phosphorus

(ii) carbon

(iii) nitrogen

(iv) sulfur

(v) iron

(e) With respect to atmospheric particulates, which of the following statements is

FALSE?

(i) Decreased particle size poses an increased human health hazard because the surface

area for adsorption of pollutants increases, as compared to an equivalent mass of larger

particles

(ii) Decreased particle size below 2.5 microns poses an increased human health hazard

because they are more easily adsorbed in the lungs

(iii) Particles larger than 10 microns in diameter are subject to sedimentation due to

gravity as their major means of removal from the atmosphere

(iv) Residence times of particles are inversely related to particle diameter

(v) The London Fog of 1952 was particularly deadly because it combined acid deposition

with soot from coal-fired power plants

9. Answer the following with a brief word, phrase, numeral, or chemical compound

A. Reason why elevated ocean temperatures result in bleaching of coral reefs.
Chlorophyll a and other pigments are killed.

B. Reason why elevated atmospheric CO₂ levels result in eventual dissolution of coral reefs.
CO₂ dissolution generates additional H⁺, pulling the CaCO₃ equilibrium toward further solubility.
C. Primary reason why hydrochlorofluorocarbons do not destroy the ozone layer

The hydrogen of the HCFC is abstracted by .OH

D. Key solid-phase component of polar stratospheric clouds forming in the Antarctic winter, that will ultimately cause ozone depletion

Nitric acid trihydrate

E. Approximate present rate of sea level rise, per year, caused by anthropogenic CO₂ emissions

3 mm/year

F. Fuel that is actually combusted in an integrated gasification combined cycle (IGCC) coal-fired power plant

H₂

G. Name given to the class of archaeobacteria that produce the third most potent greenhouse gas as a byproduct of their energy metabolism.

Methanogen

H. Type of organism that obtains energy from coupled redox equilibria, and that also is able to fix carbon.

Chemoautotroph

I. Reason why the tropospheric temperature decrease with altitude is greater in the desert

There is much less water that releases latent heat upon condensation (as the air rises)

J. Approximate rise in global sea levels likely to result from complete melting of the Greenland ice cap

7 meters

K. Chemical identity of the "atmospheric vacuum cleaner"

.OH

L. Within a plant cell, location of the protein apparatus that absorbs visible photons
membrane (outer cell membrane)

M. Gaseous sulfur-containing compound naturally produced by biological processes
DITHYOSULFATE

N. Long-chain polymer of glucose that is difficult to enzymatically degrade, in an industrial processing environment designed to ultimately produce ethanol
cellulose

O. Among the following, the gas that does not absorb IR radiation: CO_2 , H_2O , CO , N_2 , CH_4
 N_2

P. Reason why atmospheric CO_2 concentrations are higher in the Northern Hemisphere winter
Much less vegetation present to fix the CO_2

Q. Among the following, the region with highest albedo: Arctic ice cap, Brazilian rain forest, Sahara desert, Atlantic Ocean
ice cap

R. Reason why catalytic converters need to have both oxidation and reduction chambers
Must remove both, NO by reduction and CO and HC by oxidation
WATER

T. Essential reagent in the Haber-Bosch nitrogen-fixation process that is not available "from thin air"

H_2