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

NAME Answer Key

PERM # _____

PROBLEM	POINTS/POSSIBLE
1	/15
2	~~/20~~ 15
3	~~/10~~ 15
4	/15
5	/15
6	/15
7	/15
8	/15
9	/40
TOTAL	/160

Chemistry & Biochemistry 123; Environmental Chemistry
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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.

$O_2 + h\nu \rightarrow O + O^*$ k_1
$O^* + M \rightarrow O + M$ k_2
$O^* + H_2O \rightarrow 2\ {}^{\cdot}OH$ k_3

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

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

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

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

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: (or H_2O)

i) inversely dependent on M, and [M] is high

ii) required hν energy is <242 nm, and those photons do NOT penetrate

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2. Consider a photochemical smog episode in which the concentration of ozone is 40 ppb and the concentration of ·NO is 80 ppb. Under conditions of standard temperature and pressure (T = 25°C, P = 1atm), separately calculate the rates of ·NO oxidization by O_2 and by O_3, given the following information:

$2\ {\cdot}NO + O_2 \rightarrow 2\ {\cdot}NO_2$; $\quad k = 2 \times 10^{-38}\ cm^6/molecule^2\text{-sec}$
${\cdot}NO + O_3 \rightarrow {\cdot}NO_2 + O_2$; $\quad k = 2 \times 10^{-14}\ cm^3/molecule\text{-sec}$

R = 0.082 L-atm/mol-°K
Partial pressure of O_2 = 0.21 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.

$$HAc \rightleftharpoons H^+ + Ac^-$$

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

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

Since, from equation,

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

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

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 CO_2 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 [CO_2] significantly.

In the euphotic zone CO_2 is fixed by photosynthetic 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 CO_2 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 CO_2 from the atmosphere, but reaction with limestone rocks results in dissolution of Ca^{++} and HCO_3^-, which go into the ocean,

Then, in the ocean, Ca^{++} and HCO_3^- react to form H_2CO_3 which, in equilibrium w/ CO_2 + H_2O, outgases the CO_2 back to the atmosphere

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

Effect is to draw down the CO_2 concentration, because tectonic activity, under conditions of high temperature and pressure, reverses the weathering reaction, liberating CO_2.

Over geologic time, this completes 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_2O	316 ppb	120 years	296
CHF_2Cl	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 CO_2?

CO_2 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 adelitional CO_2 is low.

By contrast, CH_4, N_2O and CHF_2Cl all absorb IR in the "atmospheric window" at about 8000–10000 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.

CH_4: 1.77 ppm / 12 years $\approx$ 0.15 ppm/yr.

N_2O: 316 ppb = 0.316 ppm / 120 years $\sim$ 0.0026 ppm/yr.

CHF_2Cl: 0.00015 ppm / 12 years $\sim$ 0.0000125 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)

CH_4: 0.15 ppm/yr × 23 = 3.45

N_2O: 0.0026 × 296 = 0.77

CHF_2Cl: 0.0000125 × 1700 = 0.021

Methane

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

(5) O_3 $ROONO_2$ $\cdot OOH$ $\cdot NO$ CH_2O $\cdot NO_2$ HNO_3 C_2H_4 H_2SO_4 SO_2

0.5 each =

Primary pollutants: $\cdot NO$, C_2H_4, SO_2, ($\cdot NO_2$)

Secondary pollutants: O_3, $ROONO_2$, OOH, H_2SO_4 CH_2O, HNO_3 ($\cdot NO_2$)

(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.

i

Required atomic O produced from $\cdot NO_2$:

$\cdot NO_2 + h\nu$ ($\lambda < 400nm$) $\rightarrow$ $\cdot NO + O$

Then $O + O_2 + M \rightarrow O_3 + M + heat$

But: $O_3 + \cdot NO \rightarrow \cdot NO_2 + O_2$

So the O_3 is destroyed and cannot be built up.

ii

- hydrocarbons produce alkyl radicals by reaction w/ $\cdot OH$, and these form alkyl peroxyl radicals ($R-O-O\cdot$) after reaction w/ O_2

Then: $R-O-O\cdot + \cdot NO \rightarrow R-O\cdot + \cdot NO_2$

The $\cdot NO$ is removed as an O_3 sink and more $\cdot NO_2$ is generated for further photodecomposition $\rightarrow$ atomic O

7. What effect would doubling of the present-day CO_2 concentration have on the pH of rain that is otherwise unpolluted?
$K_H = 0.032$ M/atm; $K_a [H_2CO_3] = 4.0 \times 10^{-7}$. 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 $[CO_2] \sim 380$ ppm $= 380 \times 10^{-6}$ ATM

$K_H = [H_2CO_{3(aq)}] / P_{CO_2}$

$\rightarrow [H_2CO_3] = 1.22 \times 10^{-5} M$

Given $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, $K_a = 4 \times 10^{-7} M$

$[H^+] = [HCO_3^-]$

$[H_2CO_3] = 1.22 \times 10^{-5} M$

$\rightarrow [H^+]^2 = K_a [H_2CO_3] \rightarrow$ pH = 5.656

IF $[CO_2] = 760$ ppm, using above equations,

$\rightarrow [H_2CO_3] = 2.43 \times 10^{-5} M$

$\rightarrow$ pH = 5.501

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

$\rightarrow$ If $[SO_2]$ are significant, the pH of the acid rain will be controlled by the

$SO_2 + H_2O \rightleftharpoons H_2SO_3$ or

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ equilibria

either of these results in pH at least one full unit lower, so the acid rain problem would not be worsened by doubled $[CO_2]$.

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: $SO_4^{2-} + 2\ CH_2O + 2\ H^+ \rightarrow H_2S + 2\ H_2O + 2CO_2$
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.

Cohabiting colorful algae are killed.

B. Reason why elevated atmospheric CO_2 levels result in eventual dissolution of coral reefs.

CO_2 dissolution generates additional H^+, pulling the $CaCO_3$ equilibria toward further solubility

C. Primary reason why hydrochlorofluorocarbons do not destroy the ozone layer

The hydrogen of the HCFC is abstracted by $\cdot OH$

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 CO_2 emissions

3 mm / year

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

H_2

G. Name given to the class of archaebacteria 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"

$\cdot OH$

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

dimethylsulfate

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

S. Essential reagent in the "reforming" reactions of both coal and methane

water

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

H_2