KEY

(ANSWERS BELOW + ON FOLLOWING PAGES...)

CHEM 304
SPRING 2008
HW & LEARNING GOALS #1: Physical and Chemical Structure of the Atmosphere

1. *Physical Structure of the Atmosphere*: Identify and name the layers of the atmosphere, the boundaries between them, and answer the following questions:

a) What physical property distinguishes the layers and/or defines the boundaries? T

b) What physical/chemical processes dictate the "property" you identified in "a"?

c) What are the approximate altitudes of the boundaries between the various layers? } SEE SKETCH →

d) Which layer contains most of the air (90% by mass!)? TROPOSPHERE

e) Fill in the blanks: Vertical mixing occurs readily in the troposphere because the LAPSE RATE is (−) (+ or –). Vertical mixing is quite slow in the stratosphere because the LAPSE RATE is (+) (+ or –).

2. *Chemical Composition*: What are the three most abundant substances in the atmosphere? How much of the atmosphere (i.e. % of total) do these species comprise – to the nearest% ? N_2 (78%), O_2 (21), Ar

3. *Concentration Units*: Water is a highly variable component of air. At "saturation" (when the air is "full" of water vapor or "100% relative humidity"), there's about 20.0 Torr of water vapor present. (That is, the *partial pressure* of water at room temperature is 20.0 Torr). **i)** Convert this pressure to units of atm, bar, and mbar. **ii)** Also calculate the *mixing ratio* of water (at 0 km). } @ NTP

4. More on *Concentration Units*: The mixing ratio of ozone at the surface ($X_{O_3}^{0km}$) is about 40.0 ppb, and in the mid-stratosphere ($X_{O_3}^{30km}$) is 8.3 ppm, where the total pressure 11.5 mbar. Calculate **i)** the partial pressure of ozone, and **ii)** the *number density* (C) (in molec/cm^3) of ozone at both altitudes. (assume T = 0°C)

5. *Free Radicals*: Which of the following species are *free radicals*?

CH_3Cl, (Cl), (CH_3), (ClO), (OClO), (NO_2), HNO_3, HOCl, O_3

CH_4, CF_3Cl, (CH_3O), (OH), (HO_2), $ClONO_2$, N_2O, (NO), SO_2

6. **CHEM 104 review warning**: *Principles of Chemical Reactivity*: Fill in the blanks.

a) A "product favored reaction" (i.e. one that "goes") has a ΔG that is (−) (+ or –), and a K_{eq} value that is >1 (>, <, or equal to) one.

b) A "reactant favored reaction" (i.e. one that does not "go") has a ΔG that is (+) (+ or –), and a K_{eq} value that is <1 (>, <, or equal to) one.

7. *Free Radical Reactions*: Identify the free radicals in the reactions below and classify each reaction as "*initiation*", "*propagation*", or "*termination*". (Note that the •'s I <u>usually</u> place above free radicals have been omitted).

a) $CH_3Cl + h\nu \rightarrow \dot{Cl} + \dot{C}H_3$ INITIATION

b) $CH_3Cl + \dot{O}H \rightarrow H_2O + \dot{C}H_3$ PROPOGATION

c) $ClO^{\bullet} + O_3 \rightarrow O\dot{Cl}O + O_2$ "

d) $NO_2^{\bullet} + \dot{O}H \rightarrow HNO_3$ TERMINATION } OPPOSING RXNS...

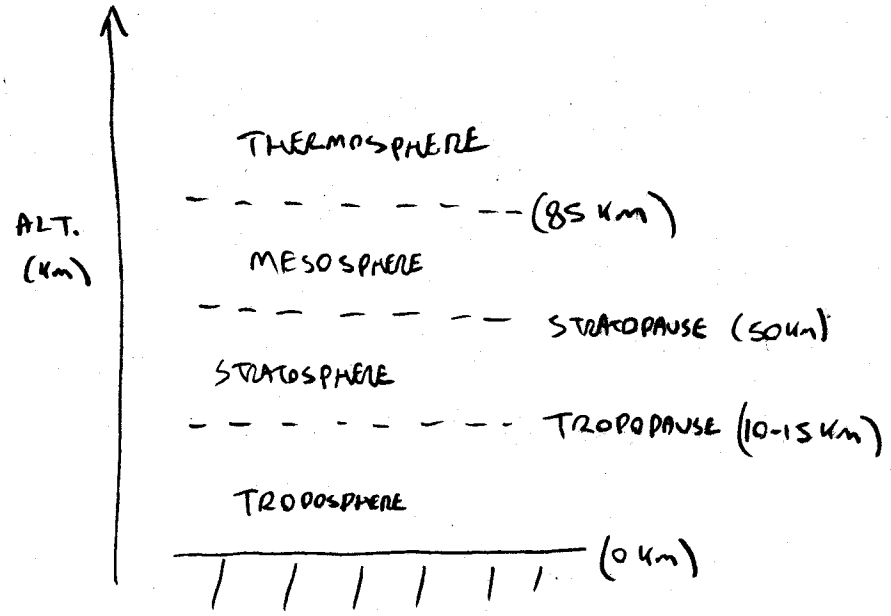
e) $HNO_3 + h\nu \rightarrow OH + NO_2$ INITIATION

f) $OH + Cl \rightarrow HOCl$ TERMINATION

304 HW# 2

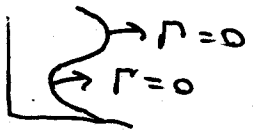
KEY ①

1. PERHAPS A SKETCH IS BEST?



a) TEMPERATURE GRADIENT (OR "LAPSE RATE") → LAPSE RATE (Γ) = 0

AT THE "PAUSES"



b) TROPOSPHERE IS HEATED FROM BELOW (BY RADIATION FROM SURFACE)

THIS MAKES $\Gamma < 0$.

STRATOSPHERE IS MA HEATED FROM WITHIN (BY O_3 PHOTOCHEMISTRY)

↑ STAY TUNED...

So $\Gamma > 0$.

c) SEE THE SKETCH ↑

d) MOST OF THE AIR (BY MASS) IS IN TROPOSPHERE.

e) VERTICAL MIXING .... troposphere ... LAPSE RATE IS ⊖.

" " Stratosphere LAPSE RATE IS ⊕.

2.

N_2 - 78%, O_2 - 21%, Ar - 1% ← (THESE ARE QUITE STABLE)

→ SUM = 100% TO NEAREST %.

3. $P_{H_2O} = 20$ Torr

$$\Rightarrow 20 \text{ Torr} \times \frac{1 \text{ atm}}{760 \text{ Torr}} = 0.026 \text{ atm}$$

$$\rightarrow 0.026 \text{ atm} \times \frac{1.01 \text{ bar}}{\text{atm}} = 0.026 \text{ bar} = 26 \text{ mbar}$$

→ a "bar" is basically = to an "atm"

4. $X_{O_3}^{0km} = 40.0 \text{ ppm} = 4.0 \times 10^{-8} \rightarrow P_{O_3}^{0km} = 1.0 \text{ atm} \times 4.0 \times 10^{-8} = 4.0 \times 10^{-8} \text{ atm}$ (or bar)

$$C_{O_3}^{0km} = 4.0 \times 10^{-8} \text{ atm} \times \left(2.7 \times 10^{19} \frac{\text{molec}}{\text{cm}^3 \cdot \text{atm}} \right) = 1.1 \times 10^{12} \frac{\text{molec}}{\text{cm}^3}$$

$X_{O_3}^{30km} = 8.3 \text{ ppm} = 8.3 \times 10^{-6}$ $P_{O_3}^{30km} = 11.5 \times 10^{-3} \text{ bar} \times 8.3 \times 10^{-6} = 9.5 \times 10^{-8} \text{ bar}$ (or atm)

$$C_{O_3}^{30km} = 9.5 \times 10^{-8} \text{ atm} \times 2.7 \times 10^{19} \frac{\text{molec}}{\text{cm}^3 \text{ atm}} = 2.6 \times 10^{12} \frac{\text{molec}}{\text{cm}^3}$$

5. YES: $\dot{Cl}$ (7e⁻), $\dot{C}H_3$ (7e⁻), $ClO\dot{}$ (13e⁻), $ClO_2\dot{}$ (19e⁻), $\dot{N}O_2$ (17e⁻)
$CH_3O\dot{}$ (13e⁻), $H\dot{O}$ (7e⁻), $H\dot{O}_2$ (13e⁻), $N\dot{O}$ (11e⁻).
(THE "·" LIES ABOVE THE ATOM W UNPAIRED e⁻)

6. a) $\Delta G < 0$ (i.e. ⊖) → $K > 1$
b) $\Delta G > 0$ (i.e. ⊕) → $K < 1$

} LOOK AT HOW THESE EQNS BEHAVE:
$\Delta G = -RT \ln K$ ← $K > 1, < 1$?
$K = \exp\left(-\frac{\Delta G}{RT}\right)$ ← $e^{+\#}$?
$e^{-\#}$?

7.
INITIATION = a, e
PROPAGATION = b, c
TERMINATION = d, f