KEY

CHEM 304
SPRING 2009
HW & LEARNING GOALS #2: Disequilibrium, kinetics and the Chapman Cycle I

1. "*Disequilibrium*" in the stratosphere: Consider the reaction $3O_2$ –> $2\,O_3$

i) $\Delta G_f°$ for O_3 is 163.4 kJ/mol, use this to calculate ΔG_{RXN} for the reaction above.

ii) Use the result from "i" to Calculate Kp from ΔG (assume 225K – T at 25km).

iii) Estimate the pressure at 25km in altitude (from the graph handed out in class), and realizing that X_{O2} =.21, calculate the partial pressure of O_2, and in turn (using Kp from ii) the partial pressure of O_3 (as predicted by EQ chemistry).

iv) Now, let's calculate mixing ratios (observed and predicted) and compare. a) To calculate "predicted" X_{O3} use the partial pressure from "iii" and the total pressure. b) To calculate "observed" use $[O_3]$ form the overhead in class ($[O_3] = 5 \times 10^{12}$ mole/cm^3, and total number density $[M] = 8.3 \times 10^{17}$ molec/cm^3). c) Do they compare well? Are you surprised? What is going on in the stratosphere that would drive the atm out of equilibrium?

2. General questions about reaction rates (*some of this is 104 review – some is new...*):

a) State the factors that affect the rate of a chemical reaction (that is non-photochemical), and which are included in the rate constant (k).

b) What factors affect the rate of a photochemical reaction, and which of these are included in a photochemical rate constant (J)? (*I will explain this a bit further in the key ...*)

c) Why does a combination reaction (e.g. *A* + *B* –> *C*) require an additional molecule ("M") to collide with the 2 reacting molecules for the reaction to occur?

d) For the reactions below: **i)** write the general expressions for the rate laws, **ii)** identify the individual reaction orders (i.e. "___ order in "A"), **iii)** state the overall reaction orders (i.e. "___ order overall), and **iv)** specify the proper units for the rate constants when concentrations are expressed in molculec/cm^3 (a.k.a. "number density").

i) A + hv –> 2 B
ii) A + B –> C + D
iii) A + B + M –> C + M*

(Note that, in general, you cannot equate reaction orders with stoichiometric reaction coefficients. However, we can do this for atmospheric reactions since they are almost always gas-phase, "elementary" (single-step) reactions).

3. The Chapman Cycle – kinetic considerations:

a) List the reactions that comprise the Chapman cycle, and write expressions for their rate laws, and label them with the net loss or gain of "odd oxygen" (i.e. in units of "Ox").

b) Add the reactions together (double #2) to show that collectively, the reactions of the Chapman cycle cause no "net" chemistry, merely a sort of "cyclical engine" that converts light to heat.

c) Calculate the rates of each reaction, using the following data:

$J_1 = 3.7 \times 10^{-27}$ sec^{-1}	$[O_3] = 5 \times 10^{12}$ molec/cm3
$k_2 = 3.0 \times 10\text{-}34$ cm^6/molec^{2}sec	$[M] = 8.3 \times 10^{17}$ molec/cm3
$J_3 = 5.4 \times 10^{-4}$ sec^{-1}	$X_O = 1.0 \times 10^{-11}$
$k_4 = 8.4 \times 10^{-16}$ cm^3/molec sec	$X_{O2} = 0.21$

d) Examine the values of the reaction rates above, what about these data justifies the notion of an "Ox" family?

e) An altitude-specific estimate of the rate constant (J_1) for step #1 in the cycle (O_2 *photolysis* in the lingo of the field) is ~10^{-11} sec.$^{-1}$ at 30 km. Use this to calculate the lifetime of O_2 (τ_{o_2}). Compare this to the lifetime calculated using reaction #2 (and data above). Is the rationale in "d" still valid?

4. Tropospheric chemistry preview: The main process by which most compounds are degraded in the lower atmosphere is by reaction with OH, via a "hydrogen abstraction" reaction, *e.g.*

$$HX + OH \rightarrow H_2O + X$$

The mixing ratio of OH (X_{OH}) is 6×10^{-14} at 0 km (and the total number density [M] is 2.7×10^{19} molec/cm^3). Complete each reaction below, and use the rate data below to calculate the lifetimes of each organic (carbon-containing) compound below (methane, propane, and formaldehyde...).

a) CH_4 + OH —> $\dot{C}H_3 + H_2O$ (k = 6.6×10^{-15} cm^3/molecule sec)

b) C_3H_8 + OH —> $\dot{C}_3H_7 + H_2O$ (k = 1.1×10^{-12} cm^3/molecule sec)

c) H_2CO + OH —> $H\dot{C}O + H_2O$ (k = 1.0×10^{-11} cm^3/molecule sec)*

↳ FORMYL

* Photochemistry is a significant H_2CO loss pathway too! Ignore this fact for now...

1\. i) $\Delta G = 2\Delta G_f(O_3) - 3\Delta G_f(O_2)$

$= 2(164.3) - 3(0) = 328.6\ \text{kJ/mol}$ → LARGE & (+)

ii) $\Delta G = -RT\ln K_P$ OR → $K_P = \exp\left(\frac{-\Delta G}{RT}\right)$ → ΔG IN J/mol

$K_P = \exp\left(\frac{-328600\ \text{J/mol}}{8.314\ \text{J/K mol} \cdot 225\text{K}}\right) = 5\times10^{-77}$ (wow!)

(THIS RXN DOES NOT GO)

iii) $P \cong 40\ \text{Torr} \approx 0.05\ \text{atm}$ $P_{O_2} = .21 \cdot 0.05 = 0.011\ \text{atm}$

$K_P = \frac{P_{O_3}^2}{P_{O_2}^3} \rightarrow P_{O_3} = \sqrt{K_P \cdot P_{O_2}^3}$

$= \sqrt{5\times10^{-77} \cdot .011^3} = 8.2\times10^{-42}\ \text{atm}$

iv) a) PREDICTED $X_{O_3} = \frac{8.2\times10^{-42}}{0.05\ \text{atm}} = 1.6\times10^{-40}$

b)

OBSERVED $X_{O_3} = \frac{5\times10^{12}}{8.3\times10^{17}} = 6.0\times10^{-6}$ ↑ 6 ppm

} OFF BY $>10^{35}$!!!!

c) THERE IS MUCHO PHOTOCHEMISTRY GOING ON → THIS DRIVES THE STRATOSPHERE WAY OUT OF EQUILIBRIUM!

2\. RATE INCREASES WHEN ... (OR VICE VERSA)

a) i) - CONCENTRATION INCREASES - RATE ~ $[A]^x$ ...

ii) - TEMPERATURE INCREASES -

iii) - VIA CATALYSTS

iv) - THERE IS ALSO AN INTRINSIC PART - I.E. SOME RXNS ARE JUST FAST!

ii) + iv) ARE REFLECTED IN THE RATE CONSTANT.

(b) $J = [h\nu][\sigma][\phi]$

- $[\sigma]$ → PROBABILITY OF ABSORPTION EXPRESSED AS AREA – $\frac{cm^2}{molec}$
- $[\phi]$ → DISSOCIATION PROBABILITY (NO UNITS – A # FROM 0→1)
- $[h\nu]$ ↑ "CONCENTRATION" OF LIGHT (ACTUALLY FLUX ~ $\frac{photons}{sec\,cm^2}$)

J HAS UNITS OF sec^{-1} (A 1ST ORDER RATE CONST..)

$$\left(\frac{photons}{cm^2 \cdot sec} \cdot \frac{cm^2}{molec} \cdot -\right) = \frac{photons}{molec \cdot sec} \sim sec^{-1}$$

↑ PHOTONS + MOLECULES NOT UNITS!

2 c) $A + B \rightarrow C$ (OR A–B)

IS AN EXOTHERMIC REACTION – ONE THAT RELEASES ENERGY → M IS NECESSARY TO COLLIDE W/ A + B TO ACTUALLY CARRY THAT E AWAY!

2 D) i) RATE = $J[A]$ → 1ST ORDER IN A, 1ST ORDER OVERALL

$J \sim sec^{-1}$

ii) RATE = $K[A][B]$ → 1ST ORDER IN A+B, 2ND ORDER OVERALL

$K \sim \frac{cm^3}{molec\,sec}$

iii) RATE = $K[A][B][M]$

1ST ORDER IN A, B, AND M → 3RD ORDER OVERALL

$K \sim \frac{cm^6}{molec^2\,sec}$

→ NOTE – RATE HAS UNITS OF $\frac{moles}{cm^3 sec}$, SO K HAS TO VARY W/ TOTAL ORDER...

Reaction	RATE	NET OX
1) $O_2 + h\nu \xrightarrow{J_1} 2O$	$J_1[O_2]$	+2
2) $O_2 + O + M \xrightarrow{K_2} O_3 + M$	$K_2[O][O_2][M]$	0
3) $O_3 + h\nu \xrightarrow{J_3} O_2 + O$	$J_3[O_3]$	0
4) $O_3 + O \xrightarrow{K_4} 2O_2$	$K_4[O][O_2]$	-2

5) DOUBLING #2 + ADDING RESULTS IN ALL O_2'S, O'S + O_3'S CANCELLING (M'S TOO!) ...

THE RESULT IS $2h\nu \rightarrow$ (heat)

REACTIONS #2/#4 ARE EXOTHERMIC.

c) 1) RATE $= J_1[O_2] =$ **6.4×10^{10} $\frac{molec}{cm^3 sec}$**

$[O_2] = X_{O_2} \cdot [M] = .21 \cdot 8.3\times10^{17} = 1.7\times10^{17}$ $\frac{molec}{cm^3}$

(J IS A VERTICAL AVE → SEE PART "e")

2) RATE $= K_2[O][O_2][M] =$ **3.5×10^{8} $\frac{molec}{cm^3 sec}$**

$[O] = 1.0\times10^{-11} \cdot 8.3\times10^{17} = 8.3\times10^{6}$ $\frac{molec}{cm^3}$

3) RATE $= J_3[O_3] =$ **2.7×10^{9} $\frac{molec}{cm^3 sec}$**

4) RATE $= K_4[O][O_3] =$ **3.5×10^{4} $\frac{molec}{cm^3 sec}$**

d) NOTE THAT REACTIONS #2 + #3 ARE MUCH FASTER - THIS LEADS TO RAPID INTERCONVERSION OF $O \rightleftarrows O_3$

3 c) $\tau_{O_2} = \frac{1}{J_1}$ (RELATIVE TO REACTION #1)

$= 10^{11}$ sec $\approx$ 3200 YEARS $\Rightarrow$ STILL LONG

AND LONGER THAN THAT ACCORDING TO #2

(0.023 sec ACCORDING TO WHAT WE DID IN CLASS...)

4. FOR ALL REACTIONS / ORGANIC CMPDS $\Rightarrow$ RATE = K [OH][HX]

SO $\rightarrow$ $\tau = \frac{1}{K[OH]}$

$[OH] = 6 \times 10^{-14} \times 2.7 \times 10^{19} \frac{molec}{cm^3} = 1.62 \times 10^{6} \frac{molec}{cm^3}$

a) $\tau_{CH_4} = \frac{1}{1.62 \times 10^{6} \frac{molec}{cm^3} \cdot 6.6 \times 10^{-15} \frac{cm^3}{molec\ sec}}$ $= 9.4 \times 10^{7}$ sec

↑ [OH] ↑ [K]

~ 3 YEARS (THAT # IS OFF...!)

b) $\tau_{C_3H_8} = \frac{1}{1.1 \times 10^{-12} \cdot 1.62 \times 10^{6}}$ $= 5.6 \times 10^{+5}$ sec (MUCH SHORTER!)

↑ PROPANE!

6.5 DAYS → REMEMBER THIS...

c) $\tau_{H_2CO} = \frac{1}{1.0 \times 10^{-11} \cdot 1.62 \times 10^{6}}$ $= 6.2 \times 10^{4}$ sec

17 HOURS

(PHOTOLYSIS OF H_2CO IS EVEN FASTER...)