

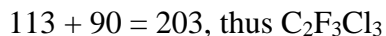
NAME: _____ STUDENT NUMBER: _____

CHEM 2800

First Midterm Test Thursday February 9, 2017
Some data and a periodic table appear on page 7
Calculators Allowed

Part A. Answer each question briefly with a few sentences or equations as necessary (5 marks each).

1. What compound is CFC-113?



2. Why is there a maximum in the temperature of the atmosphere at the stratopause?

This is where the ozone concentration is at its highest. Ozone absorbs IR radiation and keeps this portion of the atmosphere warm.

3. Name two active and three inactive forms of chlorine involved in formation of the “ozone hole.”

Active: $\dot{\text{Cl}}$ and $\dot{\text{ClO}}$

Inactive: ClONO_2 , HCl and HOCl

4. The hydroxyl radical ($\dot{\text{OH}}$) reacts with most hydrocarbons in a predictable manner. What are the likely reaction products of $\dot{\text{OH}}$ with C_3H_6 ?

$\dot{\text{OH}} + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_5\dot{\text{H}} + \text{H}_2\text{O}$ is the likely reaction. ($\dot{\text{OH}}$ usually pulls an H atom away from a hydrocarbon, making water and a hydrocarbon radical.)

5. Name three things that can happen to an electronically excited molecule such as AB^* .

Any three of: collisional deactivation, internal deactivation, fluorescence, ionization, dissociation and reaction.

6. Name four things that are necessary for the production of smog.

NO_x , sunlight, hydrocarbons (HCs), and $T > 18^\circ\text{C}$

7. Name three reasons that SO_2 in the atmosphere leads to more acidification of rain than an equal concentration of CO_2 .

1. SO_2 dissolves more in water (its K_H value is larger)
2. The acid produced (H_2SO_3) is stronger than H_2CO_3 . (its K_{a1} value is larger)
3. The H_2SO_3 may get further oxidized to H_2SO_4 , an even stronger acid. This does not happen with H_2CO_3 .

8. What is the most interesting fact you have learned so far in this course, i.e. that you did not know before?

....

Part B. Answer both questions B1 and B2.

B1. The reaction $\dot{\text{O}}\text{H} + \text{H}_2\text{S} \xrightarrow{k} \dot{\text{S}}\text{H} + \text{H}_2\text{O}$ has $A = 6.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ and $E_a = 623 \text{ J mol}^{-1}$.

(a) Calculate the rate constant for this reaction at 15°C .

$$\begin{aligned} k &= A e^{\frac{-E_a}{RT}} \\ &= 6.0 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} e^{\frac{-623 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (15 + 273.15) \text{ K}}} \\ &= 4.63 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \end{aligned}$$

(b) In urban air, typical concentrations are $[\dot{\text{O}}\text{H}] = 10^6 \text{ molec cm}^{-3}$ and $[\text{H}_2\text{S}] = 0.20 \text{ ppbv}$. Calculate the reaction rate (in $\text{molec cm}^{-3} \text{ s}^{-1}$) assuming the total pressure is 1.00 bar and $T = 15^\circ\text{C}$.

$[\text{H}_2\text{S}] = 0.20 \text{ ppbv} = 0.20 \times 10^{-9} (1 \text{ bar}) = 0.20 \times 10^{-9} \text{ bar} = 0.20 \times 10^{-4} \text{ Pa}$. This needs to be converted into molec cm^{-3} :

$$\begin{aligned} pV &= nRT \\ \frac{n}{V} &= \frac{p}{RT} \\ &= \frac{0.20 \times 10^{-4} \text{ Pa}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} (15 + 273.15) \text{ K}} \\ &= 8.35 \times 10^{-9} \text{ mol m}^{-3} \\ &\times \frac{6.02 \times 10^{23} \text{ molec mol}^{-1}}{(100)^3 \text{ cm}^3 \text{ m}^{-3}} = 5.03 \times 10^9 \text{ molec cm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{Thus, rate} &= k[\dot{\text{O}}\text{H}][\text{H}_2\text{S}] \\ &= 4.63 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (10^6 \text{ molec cm}^{-3}) (5.03 \times 10^9 \text{ molec cm}^{-3}) \\ &= 2.33 \times 10^4 \text{ molec cm}^{-3} \text{ s}^{-1} \end{aligned}$$

B2. (a) Calculate the atmospheric pressure (in bar) at the top of Mount MacDonald in the Yukon, which is at an altitude of 2760 m. Use an appropriate temperature. Assume air is 20% O₂, 79% N₂ and 1% Ar, that the surface temperature is 15.0°C, p₀ = 1.00 bar, and that the lapse rate is -6.5 K km⁻¹.

At 2760 m, the temperature is 15°C - 2.76 km(6.5 K/km) = -2.94°C. The average temperature from 0 - 15 km is therefore (-2.94 + 15.0)/2 = 6.03°C = 279.2 K.

The average molecular weight is M = 0.20(32.00 g/mol) + 0.79(28.00 g/mol) + 0.01(40.0 g/mol) = 28.92 g/mol = 0.02892 kg/mol.

$$\begin{aligned} p &= p_0 \exp\left(\frac{-Mg_0 z}{RT}\right) \\ &= 1.00 \text{ bar} \exp\left(\frac{-0.02892 \text{ kg mol}^{-1}(9.80 \text{ m s}^{-2})(2792 \text{ m})}{8.314 \text{ J K}^{-1}\text{mol}^{-1}(279.2 \text{ K})}\right) \\ &= 1.00 \text{ bar} (0.711) \\ &= 0.711 \text{ bar} \end{aligned}$$

(b) Calculate the concentration of air molecules at 2760 m. Use the temperature at this 2792 m, not the average temperature from 0 to 2792 m, to do this calculation.

$$\frac{v}{V} = \frac{p}{RT} = \frac{0.711 \text{ bar} \left(\frac{10^5 \text{ Pa}}{\text{bar}}\right)}{8.314 \text{ J K}^{-1}\text{mol}^{-1}(-2.94 + 273.15)\text{K}} = 31.6 \text{ mol m}^{-3}$$

$$31.6 \text{ mol m}^{-3} \times \frac{6.02 \times 10^{23} \text{ mol}^{-1}}{\frac{10^6 \text{ cm}^3}{\text{m}^3}} = 1.91 \times 10^{19} \text{ cm}^{-3}$$

(c) In the stratosphere, COS_(g) sources total 1.2 Tg y⁻¹. The lifetime of COS in the stratosphere is 10.0 y. Calculate the concentration of COS in the stratosphere (in ppbv), given that the density of COS under stratospheric conditions is 0.164 kg m⁻³ and that the volume of the stratosphere is 1.1 × 10¹⁸ m³.

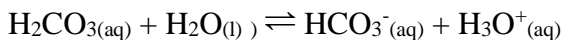
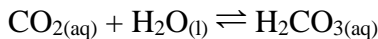
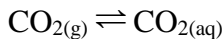
$$Q = \tau P = 10 \text{ y}(1.2 \times 10^{12} \text{ g y}^{-1}) = 1.2 \times 10^{13} \text{ g}$$

$$V_{\text{COS}} = \frac{Q}{\rho} = \frac{1.2 \times 10^{10} \text{ kg}}{0.164 \text{ kg m}^{-3}} = 7.32 \times 10^{10} \text{ m}^3$$

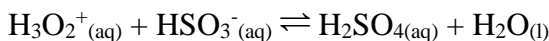
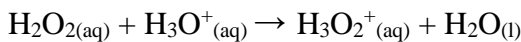
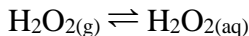
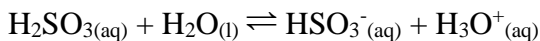
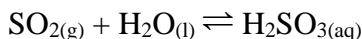
$$[\text{COS}] = \frac{7.32 \times 10^{10} \text{ m}^3}{1.1 \times 10^{18} \text{ m}^3} \times 10^9 \text{ ppbv} = 0.67 \text{ ppbv}$$

Part C. Answer either C1 or C2 (20 marks each). If you manage to do both, I will use the better of the two to calculate your mark.

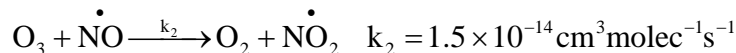
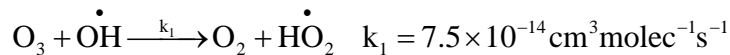
C1. (a) Show three reactions, beginning with $\text{CO}_{2(g)}$, that explain why water in contact with the atmosphere is acidic.



(b) Show how $\text{SO}_{2(g)}$ gets oxidized to $\text{H}_2\text{SO}_{4(aq)}$ by $\text{H}_2\text{O}_{2(g)}$ in a wet atmosphere (five reactions)



(c) Stratospheric ozone is destroyed primarily by two reactions:

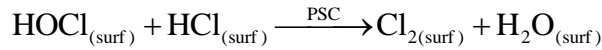
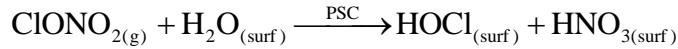
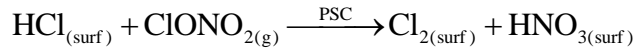


Calculate the lifetime (in s) of ozone if $[\dot{\text{O}}\text{H}] = 10^7 \text{ molecule cm}^{-3}$ and

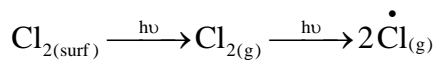
$$[\dot{\text{N}}\text{O}] = 10^8 \text{ molecule cm}^{-3}$$

$$\begin{aligned} \tau_{\text{O}_3} &= \frac{[\text{O}_3]}{k_1[\dot{\text{O}}\text{H}][\text{O}_3] + k_2[\dot{\text{N}}\text{O}][\text{O}_3]} = \frac{1}{k_1[\dot{\text{O}}\text{H}] + k_2[\dot{\text{N}}\text{O}]} \\ &= \frac{1}{7.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (10^7 \text{ molec cm}^{-3}) + 1.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (10^8 \text{ molec cm}^{-3})} \\ &= 4.44 \times 10^5 \text{ s} \end{aligned}$$

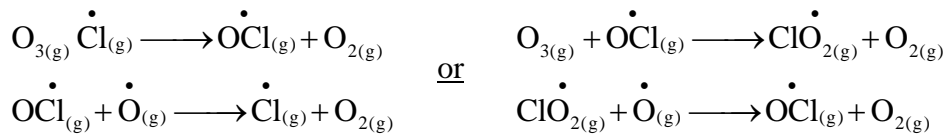
- C2. (a) [5] Show three reactions that convert inactive forms of chlorine to active forms on the surfaces of polar stratospheric cloud particles.



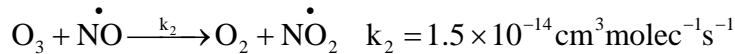
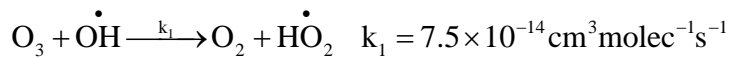
- (b) [5] Show two reactions that cause active chlorine species on the surfaces of polar stratospheric cloud particles to enter the gas phase. Also show how one of these species destroys ozone in a catalytic cycle (two reactions).



Then:



- (c) Stratospheric ozone is destroyed primarily by two reactions:



Calculate the lifetime (in s) of ozone if $[\dot{\text{OH}}] = 10^7 \text{ molecule cm}^{-3}$ and

$$[\dot{\text{NO}}] = 10^8 \text{ molecule cm}^{-3}$$

$$\begin{aligned} \tau_{\text{O}_3} &= \frac{[\text{O}_3]}{k_1[\dot{\text{OH}}][\text{O}_3] + k_2[\dot{\text{NO}}][\text{O}_3]} = \frac{1}{k_1[\dot{\text{OH}}] + k_2[\dot{\text{NO}}]} \\ &= \frac{1}{7.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (10^7 \text{ molec cm}^{-3}) + 1.5 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} (10^8 \text{ molec cm}^{-3})} \\ &= 4.44 \times 10^5 \text{ s} \end{aligned}$$