NAME:

75 MINUTES; HAND IN YOUR SHEETS OF NOTES WITH THE EXAM; ASK FOR EXTRA PAPER IF NEEDED. MAKE (AND STATE) ANY REASONABLE ASSUMPTIONS NECESSARY TO GET AN ANSWER IN ADDITION TO THOSE GIVEN. CHECKING WHETHER THE ANSWER MAKES SENSE IS NOT REQUIRED HERE BUT MAY HELP YOU EARN PARTIAL CREDIT IF YOU WENT WRONG SOMEWHERE.

PROBLEM 1 (20 pts):

Estimate the mass concentration (kg m^{-3}) and molarity of nitrate, NO_3^-, in a stream if a 10 L sample of stream water is found to contain 0.3 g nitrate.

0.3 g / 10 L = 0.03 g / L = 30 g m^{-3} = 0.03 kg m^{-3} (mass concentration)
MW nitrate: 14 + 3*16 = 62 g/mol
0.03 g / L / 62 g / mol = 4.8 * 10^{-4} mol / L (molarity)

PROBLEM 2 (45 pts):
A city has a rectangular shape extending 10 km in the x direction and 5 km in the y direction. Use a 0-D model to estimate the steady-state NO concentration in the city if the upwind concentration is 1 ppb and the city emits NO at a rate of $4 * 10^{-9}$ mol m^{-2} s^{-1}.
Assume that there is a steady wind in the x direction with an average velocity of 3 m s^{-1}; the boundary layer height is 500 m with an average temperature of 280 K and pressure of 10^5 Pa; and that NO is destroyed in a first-order reaction with a rate constant k = 2 d^{-1}.

Mass balance for NO (assuming air is incompressible here):
V dC/dt = Q (C_in - C_out) + E - kCV

V is equal to (10000 m)(5000 m)(500 m) = 2.5E10 m^3
Q is equal to vA = (3 m s^{-1})(500 m)(5000 m) = 7.5E6 m^3 s^{-1} (A is the YZ cross section)
E is equal to the emission rate times the city surface area: ($4 * 10^{-9}$ mol m^{-2} s^{-1})(10000 m)(5000 m) = 0.2 mol s^{-1}
convert C_in from mole fraction to units of mol m^{-3} via the ideal gas law: n/V = P/(RT) = (10^5)/(8.314)(280) = 43 mol air m^{-3}, so C_in = 4.3E-8 mol NO m^{-3}.
in seconds, k is 2/86400 = 2.3E-5 s^{-1}

Setting the rate of change equal to zero and C_out = C (0-D assumption), we have
0 = Q (C_in - C) + E - kCV
so
C = (Q C_in + E) / (Q + kV) = 6.46E-8 mol NO m^{-3}
or 1.5 ppb.

PROBLEM 3 (35 pts):

A sewer treatment plant measures an $H_2S(g)$ partial pressure of 10^{-7} atm. Find the concentrations of $H_2S(aq)$, $HS^{-}(aq)$, and $S^{-2}(aq)$ assuming equilibrium and pH = 6. The Henry's Law constant for H_2S is 9.26 atm/M, while pK_{a1} and pK_{a2} for H_2S are 6.99 and 12.92 respectively.

At equilibrium, $[H_2S(aq)] = [H_2S(g)]/K_H = 1.08E\text{-}8$ M
$[HS^{-}(aq)] = (K_{a1})[H_2S(aq)]/[H+] = 1.11E\text{-}9$ M
$[S^{-2}(aq)] = (K_{a2})[HS^{-}(aq)]/[H+] = 1.33E\text{-}16$ M

GIVEN INFORMATION

1 m^3 = 1000 L, 1 mg = 10^{-3} g, 1 μg = 10^{-6} g

T(degK) = T(degC) + 273.15, 1 atm = 101325 Pa

$$\mathrm{MW}_i = \frac{\text{mass i}}{\text{mols i}} = \sum_{k=1,K} n_k \mathrm{AW}_k, \quad \mathrm{FW} = \sum_{k=1,K} y_i \mathrm{MW}_i$$

PV=nRT where R = 0.08206 L atm mol^{-1} K^{-1} or 8.314 m^3 Pa mol^{-1} K^{-1}

$$\rho_{air} = \frac{\text{mass air}}{\text{volume air}} = \frac{n_{air} \times MW_{air}}{V_{air}} = \frac{n_{air}}{V_{air}} \times MW_{air} = \frac{P}{RT} \times MW_{air}$$

$$M_i = \frac{\text{mols i}}{\text{L m}} = \frac{\text{mass}_i / \mathrm{MW}_i}{V_w} = \frac{m_i}{\mathrm{MW}_i}$$

$$\mathrm{pH} = -\log(M_{H^+}), \mathrm{pOH} = -\log(M_{OH^+}), \mathrm{pH} + \mathrm{pOH} = 14 \text{ at } 25°\mathrm{C}$$

$$y_i = \frac{\text{mols i}}{\text{mols t}} \approx \frac{\text{mass}_i / MW_i}{\rho_m \times V_m \,/\, MW_m} \quad \text{and} \quad \sum_{i=1,I} y_i = 1$$

$$\mathrm{P}_i = y_i \mathrm{P} \quad \text{and} \quad \sum_{i=1,I} P_i = P$$

AW of elements in g/mol: 1 for H, 12 for C, 14 for N, 16 for O, 31 for P, 32 for S

Density of pure water at 1 atm and 4°C = 1000 kg/m^3

$$\frac{d}{dt}\int_{cv} \rho \, d\cancel{V} = -\int_{cs} \rho \, V(A) \cdot n \, dA \quad \text{and} \quad \frac{d}{dt}\int_{cv} \rho \, d\cancel{V} = \frac{dm}{dt}$$

$$\int_{cs} \rho \, V(A) \cdot n \, dA = -\int_{cs,in} \rho \, V(A) \, dA + \int_{cs,out} \rho \, V(A) \, dA = \sum_{cs,in} \rho \, \bar{V} A - \sum_{cs,out} \rho \, \bar{V} A = \sum_{cs,in} \dot{m} - \sum_{cs,out} \dot{m}$$

$$R_i = \pm \sum_{j=1,J} \left[k_j \cancel{V} \left(\prod_{h=1,H} C_{i,h} \right) \right] \qquad K = \frac{\prod_{h=1,H \text{ products}} [C_{i,h}]^{c^*}}{\prod_{h=1,H \text{ reactants}} [C_{i,h}]^{c^*}}$$

$$K = 10^{-pK} \qquad \sum_{i=1,I} n_{i,j^*} = \sum_{i=1,I} n_{i,j^o}$$

$$\mathrm{HA_{aq}} \Leftrightarrow H^+_{\mathrm{aq}} + \mathrm{A}^-_{\mathrm{aq}} \qquad A_a B_{b_s} \Leftrightarrow \mathrm{aA}^+_{\mathrm{aq}} + \mathrm{bB}^-_{\mathrm{aq}}$$

$$A_{\mathrm{aq}} \Leftrightarrow A_{\mathrm{ads}} \ \textbf{or} \ A_g \Leftrightarrow A_{\mathrm{ads}} \qquad A_a B_{b_{(\mathrm{aq})}} \Leftrightarrow A_a B_{b_{(g)}}$$