

PRINCIPLES OF GEOCHEMISTRY
GEOL 423
PROBLEM SET #2 – ANSWERS
FALL 2009

Problem 1:

a) $0.001 \text{ ppm NH}_3 = 0.001 \text{ moles}/10^6 \text{ moles NH}_3 \rightarrow p_{\text{NH}_3} = 0.001 \times 10^{-6} \text{ atm} = 10^{-9} \text{ atm}$

b) $\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g}) \leftrightarrow 2\text{NH}_3(\text{g}) + 3/2\text{O}_2(\text{g})$

c) $\Delta G_r^0 = 2\Delta G_f^0(\text{NH}_3) + 3/2\Delta G_f^0(\text{O}_2) - 3\Delta G_f^0(\text{H}_2\text{O}) - \Delta G_f^0(\text{N}_2)$
 $\Delta G_r^0 = 2(-3.94) + 3/2(0) - 3(-54.636) - (0) = 156.028 \text{ kcal mol}^{-1}$

$$\log K = \frac{-\Delta G_r^0}{2.3025RT} = \frac{-156028}{2.3025(1.987)(298.15)} = -114.36$$

$$K = 10^{-114.36}$$

d) $p_{\text{O}_2} = 0.21 \text{ atm}$; $p_{\text{N}_2} = 0.78 \text{ atm}$; $p_{\text{H}_2\text{O}} = 0.001 \text{ atm}$

$$10^{-114.36} = \frac{P_{\text{NH}_3}^2 P_{\text{O}_2}^{3/2}}{P_{\text{N}_2} P_{\text{H}_2\text{O}}^3}$$

$$10^{-114.36} = \frac{P_{\text{NH}_3}^2 (0.21)^{3/2}}{(0.78)(0.01)^3}$$

$$P_{\text{NH}_3}^2 = 10^{-119.45}$$

$$p_{\text{NH}_3} = 10^{-59.73} \text{ atm}$$

e) The above value is much less than the measured value of 10^{-9} atm and so NH_3 cannot be in equilibrium with major gases in the atmosphere. Note: if you wrote the reaction in the opposite direction that I did, or multiplied all stoichiometric coefficients by a constant factor, that is fine, as long as the signs and magnitudes of ΔG_r^0 and $\log K$ are consistent.

At equilibrium, p_{NH_3} , should be $2 \times 10^{-19} \text{ atm}$. Instead, it is much higher at $3 \times 10^{-7} \text{ atm}$, so it is not controlled by chemical equilibrium. It is probably in a steady-state condition.

Problem 2:

$$F = \frac{A}{\tau}$$

Hydrogen sulfide (H_2S)

$$A = (5 \times 10^{11} \text{ mol mol}^{-1})(5.21 \times 10^{21} \text{ g})(34.08 \text{ g mol}^{-1}/29 \text{ g mol}^{-1}) = 3.06 \times 10^{11} \text{ g}$$

$$\tau = 1 \text{ days} \times (1 \text{ year}/365 \text{ days}) = 0.00274 \text{ years}$$

$$F = 3.06 \times 10^{11} \text{ g}/0.00274 \text{ yrs} = 1.12 \times 10^{14} \text{ g yr}^{-1}$$

Ammonia (NH₃)

$$A = (10^{-9} \text{ mol mol}^{-1})(5.21 \times 10^{21} \text{ g})(17.03 \text{ g mol}^{-1}/29 \text{ g mol}^{-1}) = 3.05 \times 10^{12} \text{ g}$$

$$\tau = 2 \text{ days} \times (1 \text{ year}/365 \text{ days}) = 0.00548 \text{ years}$$

$$F = 3.05 \times 10^{12} \text{ g}/0.00548 \text{ yrs} = 5.572 \times 10^{14} \text{ g yr}^{-1}$$

Carbon disulfide (CS₂)

$$A = (2 \times 10^{-11} \text{ mol mol}^{-1})(5.21 \times 10^{21} \text{ g})(76.143 \text{ g mol}^{-1}/29 \text{ g mol}^{-1}) = 2.731 \times 10^{11} \text{ g}$$

$$\tau = 40 \text{ days} \times (1 \text{ year}/365 \text{ days}) = 0.10968 \text{ years}$$

$$F = 2.731 \times 10^{11} \text{ g}/0.10968 \text{ yrs} = 2.492 \times 10^{12} \text{ g yr}^{-1}$$

Methyl chloride (CH₃Cl)

$$A = (7 \times 10^{-10} \text{ mol mol}^{-1})(5.21 \times 10^{21} \text{ g})(50.49 \text{ g mol}^{-1}/29 \text{ g mol}^{-1}) = 6.35 \times 10^{12} \text{ g}$$

$$\tau = 30 \text{ days} \times (1 \text{ year}/365 \text{ days}) = 0.082 \text{ years}$$

$$F = 6.35 \times 10^{12} \text{ g}/0.082 \text{ yrs} = 7.74 \times 10^{13} \text{ g yr}^{-1}$$

Problem 3: This question is to be answered on the basis of the residence time of the trace gas. On the one hand, a large τ value implies that the gas will remain in the atmosphere a long time; on the other hand, a large τ value implies the gas may not be very reactive (i.e., it is relatively inert) and therefore not too dangerous. A small τ value implies a gas that will not remain in the atmosphere for very long, but it will be highly reactive and will be of concern as long as it is present. Perhaps the most dangerous gas would be one of moderate reactivity and moderate residence time in the atmosphere, i.e., of intermediate τ value.

The gases with the highest τ in the table are nitrous oxide and carbon dioxide. These will stick around in the atmosphere a long time, but may not be very chemically reactive. The gases with the shortest residence time in Table 2.3 are dimethyl sulfide, hydrogen sulfide and ammonia; these are extremely reactive, but won't be a long-term hazard because they are quickly removed from the atmosphere. Species with intermediate τ may be both reactive and will remain in the atmosphere sufficiently long times to be a hazard.

Problem 4: This problem employs the relationship $K_{H,i} = \left(\frac{c_i}{P_i} \right)$

Ammonia: $p_{\text{NH}_3} = 10^{-9} \text{ atm}$; $K_{\text{H}} = 90 \text{ mol L}^{-1} \text{ atm}^{-1}$

$$c_{\text{NH}_3} = K_{\text{H}} \cdot p_{\text{NH}_3} = (90)(10^{-9}) = 9.0 \times 10^{-8} \text{ mol L}^{-1}$$

Carbon monoxide: $p_{\text{CO}} = 1.0 \times 10^{-7} \text{ atm}$; $K_{\text{H}} = 0.001 \text{ mol L}^{-1} \text{ atm}^{-1}$

$$c_{\text{CO}} = K_{\text{H}} \cdot p_{\text{CO}} = (0.001)(1.0 \times 10^{-7}) = 1.0 \times 10^{-10} \text{ mol L}^{-1}$$

Oxygen: $p_{\text{O}_2} = 0.21 \text{ atm}$; $K_{\text{H}} = 0.0015 \text{ mol L}^{-1} \text{ atm}^{-1}$

$$c_{\text{O}_2} = K_{\text{H}} \cdot p_{\text{O}_2} = (0.0015)(0.21) = 3.15 \times 10^{-4} \text{ mol L}^{-1}$$

Problem 5: The lower the pK_{a} , the stronger the acid. HCl is such a strong acid, a pK_{a} value cannot be accurately determined. Otherwise:

$$pK_a(\text{HF}) = 3.2; pK_a(\text{acetic acid}) = 4.75; pK_{a,1}(\text{H}_3\text{PO}_4) = 2.1; pK_a(\text{H}_3\text{BO}_3) = 9.2$$

so



Problem 6: Here we use the barometric law: $p_{\text{Ne},z} = p_{\text{Ne},0}\exp(-z/H)$

We also have: $p_{\text{Ne},0} = 18.18 \times 10^{-6}$ atm; $z = 52$ km; $H = 8.4$ km so

$$p_{\text{Ne},z} = 18.18 \times 10^{-6} \exp(-52/8.4) = 3.72 \times 10^{-8} \text{ atm}$$

Andrews et al. indicate that $H = 8.4$ km is not strictly valid beyond the troposphere, but we use it here just for illustrative purposes.