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Final Examination for CHMB55 Environmental Chemistry

Date: April 12, 2014, 19:00 to 22:00

Maximum: 100 marks

Aquatic Chemistry (19)

1. Balance each of the following chemical equations using water, protons and electrons (3)



2. What is a redox reaction? (1)

3. Which of these reactions is **not** a redox reaction? (1)

4. What is a pH? (1)

5. Which of these reaction equilibria does **not** depend on pH? (1)

6. What is a pe? (1)

7. Does pe increase or decrease as a system becomes more reducing? (1)

8. Does the electron activity increase or decrease as a system becomes more oxidizing? (1)

9. What controls the highest and lowest pe values that can be maintained in an aqueous system? (2)

If you were to draw a pe/pH diagram for the Fe/H₂O/O₂ system based on the above equations, which of these equations would lead to:

10. a line that is parallel to the pH axis? (1)

11. a line that is parallel to the pe axis? (1)

12. a line, the position of which depends on the total amount of iron in the system? (1)

13. the line with the steepest slope? (1)

14. a line that does not appear in the final version of the pe/pH diagram? (1)

15. Explain your answer to question 14. (2)

Greenhouse Effect (12)

16. In what region of the electromagnetic spectrum do the sun and Earth emit radiation, respectively? (1)

17. Name the two types of vibrations that can occur within a molecule. (2)

18. What is the relationship between these vibrations and the global green house effect? (2)

19. What are the two most abundant molecules in the global atmosphere? Explain why they do not contribute to the global green house effect. (2)

20. What is the "atmospheric window"? (2)

21. Assume you had to design the worst possible greenhouse gas (high atmospheric residence time, high absorption efficiency of IR light). Suggest a molecular structure and explain your choice. (3)

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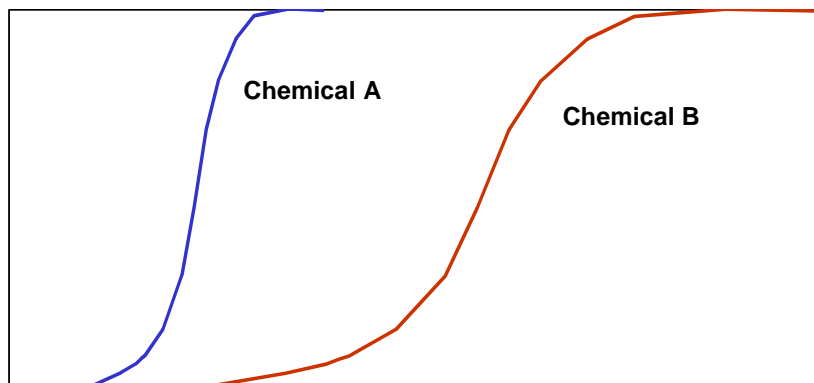
Atmospheric Chemistry and Climate Change (16)

A proposed geo-engineering approach to slow the rate of climate warming involves the injection of sulphur dioxide into the stratosphere.

22. What is the stratosphere? (1)
23. Why is it called the **stratosphere**? (1)
24. Sulphur dioxide is oxidized to sulphuric acid in the atmosphere. In the troposphere there are two pathways in which the sulphur dioxide can be oxidized. Which of these two pathways will be dominant in the stratosphere and why? (2)
25. Write down the detailed reaction scheme for the oxidation of sulphur dioxide in the stratosphere. (4)
26. Why would injection of sulfur dioxide to the stratosphere aid in slowing down global warming? (2)
27. Why is it necessary to inject the sulfur dioxide to the stratosphere (as opposed to the troposphere)? (2)
28. Why would it need to be done repeatedly? (1)
29. If humankind starts injecting sulfur dioxide into the stratosphere, we are committed to doing so for a long time. Explain why. (2)
30. Name a non-anthropogenic source of sulphur dioxide to the stratosphere. (1)

Toxicology (8)

Two chemicals were tested for their toxicity to a fish species. When the results were plotted, the following curves were obtained:



31. What do you call these sorts of relationships? (1)
32. Redraw the graph in your exam booklet and label the two axis of the plot appropriately. (2)
33. What is an LC50? Show graphically how you would establish the LC50 for chemicals A and B from the plot. (2)
34. Which one of these two chemicals is more toxic than the other? (1)
35. What does it mean that the curve for chemical A is steeper than the curve for chemical B? (2)

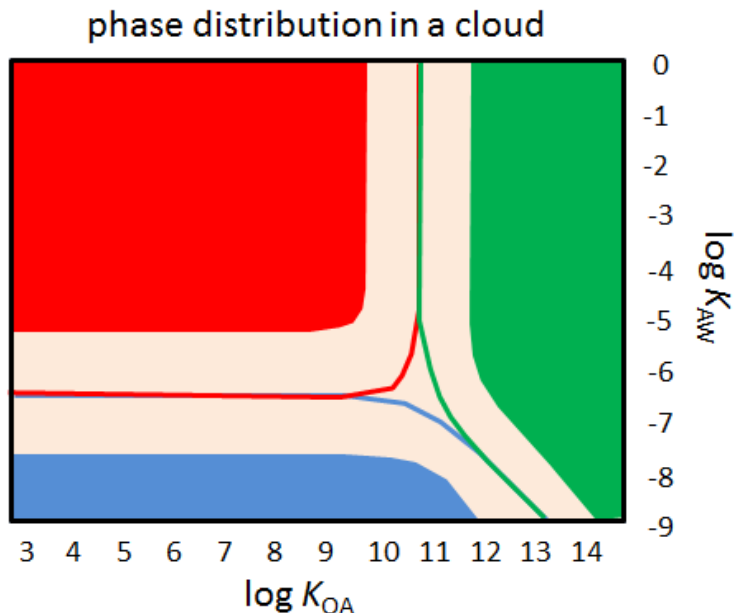
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Environmental Phase Distribution of Organic Chemicals (31)

The figure below shows a map indicating phases of preferential phase distribution in a cloud. In the plot, the colour red and the subscript A refers to the gas phase, the colour blue and the subscript W refers to the aqueous phase, and the colour green and the subscript O refers to the particulate organic matter phase. Chemicals with partitioning properties falling into areas with solid colouring are partitioning at least 90 % into one of the three phases. The coloured lines indicate 50 % partitioning into a phase.



36. Define the axis titles $\log K_{AW}$ and $\log K_{OA}$ in this plot. (2)

37. Deduce the relative volumes of air, water and particulate organic matter in the cloud from the figure, i.e. the volume ratios V_W/V_A and V_O/V_A . (5)

38. How would the figure's appearance change, if the abundance of particulate organic matter in the cloud were increased? (2)

39. What process could lead to an increase in the particulate organic matter in the atmosphere? (1)

The table below lists the partitioning properties of several polychlorinated dibenzo-para-dioxins (PCDDs). The $\log K_{XY}$ values are for 25 °C.

	$\log_{10} K_{AW}$	$\log_{10} K_{OW}$	$\log_{10} K_{OA}$
2-MCDD	-2.38	5.20	7.78
1,2,3,4-TCDD	-2.92	6.46	9.78
1,2,3,7-TCDD	-2.81	6.60	9.83
1,3,6,8-TCDD	-2.75	6.56	9.71
2,3,7,8-TCDD	-2.46	6.88	9.81
OCDD	-3.28	8.32	12.30

40. Describe and explain the trends in $\log K_{OW}$ and $\log K_{OA}$ between the MCDD, the TCDDs and the OCDD. (2)

41. Draw the molecular structure of the four TCDDs. (2)

42. Rank these four compounds in the order of increasing toxicity and explain your ranking. (2)

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43. Redraw the map in your exam booklet and locate the six PCDDs on the chemical partitioning space map and briefly indicate how the PCDDs will partition in a cloud. (3)
44. How would you expect the $\log K_{AW}$ and $\log K_{OA}$ values for these six PCDDs to change when the temperature is lower than 25 °C? (2)
45. Using the partitioning map for illustration, indicate with arrows how the phase distribution of the PCDDs in the cloud would change at lower temperature. Explain in words what it means. (3)
46. Based on the locations of the PCDDs on the partitioning space for a cloud, speculate on the deposition processes that these PCDDs will experience at different temperatures. How would you expect the atmospheric lifetimes of the PCDDs to vary with their degree of chlorination? (3)
47. Atmospheric lifetimes are not only controlled by deposition, but also by degradation. Speculate on how the rate of atmospheric degradation of the PCDDs might change with their degree of chlorination. Based on this, re-evaluate your answer to question 48 on how you would expect the atmospheric lifetime of the PCDDs to vary with their degree of chlorination. (2)
48. Would you expect any of these PCDDs to be ozone-depleting substances? Explain your answer. (2)

Bioaccumulation (14)

An experiment to determine the BCF of a chemical involves an aquarium:

49. What does BCF stand for? Define it using words and an equation. (2)
50. The aquarium is 50 cm wide and 100 cm long. It is filled with water to a depth of 20 cm. The concentration of suspended solids in the water is 2 mg/L, whereby half of these solids are made up of organic matter. Calculate the volumes of water and of suspended organic matter in the aquarium in units of L. Indicate what assumption you made about the density of suspended organic matter and why. (2)
51. Calculate the distribution of 2-MCDD, 2,3,7,8-TCDD and OCDD between water and suspended organic solids at equilibrium, assuming that the organic matter has partitioning properties similar to octanol. (4)
52. For each of these three chemicals, indicate the factor by which the calculated BCF differs from the correct BCF, if you use the total water concentration instead of the truly dissolved water concentration. (3)
53. Two types of mechanism contribute to enrichment of chemicals in a phase. What are they called? (2)
54. Bioconcentration is an example of which one of these mechanisms? (1)