

EEC 503 Spring 2013

REVIEW 1: BASIC KINETIC CONCEPTS

1. Why are chemical reactions important to energy, environmental and process engineering? Name as many reasons as you can think of.

2. What is a chemical reaction?

3. What do we mean by reaction stoichiometry? What does stoichiometry represent? What is the convention used for stoichiometric coefficients of products, reactants, inerts?

4. What is a mole? What is the relationship between a kmol and a mol? What is the relationship between a lbmol and a mol?

Consider a single reaction system and answer questions 5-7.

5. Progress of a single reaction of known stoichiometry can be represented by a molar extent of reaction. What is the relationship between the moles of reactants, products and inerts at some state of the system when extent of reaction is nonzero, the initial moles of each component in the system, the stoichiometric coefficients and reaction extent?

6. Relate the molar extent of reaction to the fractional conversion of the limiting reactant, its initial moles and its stoichiometric coefficient. What is the limiting reactant?

7. What is the relationship between mole fraction of products and reactants and reaction extent?

8. Extend the relationship developed in answering question 5. to multiple reactions consisting of R independent reactions between S species?

9. In a set of R' stoichiometric reactions between S species how would you determine the set R of independent reactions?
10. What is the rate of reaction? What does the rate of reaction depend on? What form can the rate dependence on concentration of reactants and products take?
11. What temperature dependence does the rate of reaction exhibit? What is the meaning of the activation energy for the reaction? Can it be always defined?
12. What is the Arrhenius form of the rate constant? What is the meaning of the activation energy in the Arrhenius form.
13. Which reaction rate constant increases more rapidly with temperature, the one with lower or higher activation energy?
14. How can an n -th order reaction rate be represented? If (mol/L) units are used for concentration and time is measured in seconds what are the units for the rate constant?
15. Can the temperature and composition dependence term be separated in reaction rates that follow the Langmuir-Hinshelwood (Hougen-Watson) form? Can an activation energy be defined for the rate from of that type?
16. What is molar internal energy? What is it a function of?
17. How is molar enthalpy defined? What about partial molar enthalpy? What information is needed to calculate it at a given temperature and composition?
18. What is the standard heat of reaction?

19. What is molar Gibbs free energy in terms of molar enthalpy and entropy?
20. What is the thermodynamic condition for equilibrium in a reactive system?
21. How is the thermodynamic equilibrium constant defined?
22. How is the standard Gibbs free energy for reaction calculated and how does it relate to the equilibrium constant?
23. What is Van't Hoff's equation for variation of equilibrium constant with temperature?
24. How can one calculate the heat of reaction as a function of temperature?
25. Does the equilibrium constant have units?
26. How does one relate activity to mole fraction? Activity to concentration?
27. Show using customary notation how to calculate the equilibrium conversion of SO₂ reacting with air at 25°C and at 600°C and P= 1 atm for a feed that contains: i) stoichiometric ratio of reactants only, ii) stoichiometric ratio of reactants when using air as oxygen source, iii) very large excess of air . For which of these three cases would equilibrium conversion be the highest? Explain why!
28. What would happen to the equilibrium conversion in problem 27 above if you: i) lowered the temperature to 200°C ; ii) if you raised the pressure of operation to 100 atm.
29. What is the kinetic definition of equilibrium? What constraint does that impose on the reaction forms for the reverse and forward reactions?

30. If Arrhenius form is used to represent the rate constant k_c ($(\text{mol/L})^{1-n} \text{ s}^{-1}$) and the rate constant for the same gas phase reaction k_p ($\text{mol/L atm}^{-n} \text{ s}^{-1}$), what is the relationship between k_{c0} and k_{p0} and E_c and E_p ? Assume ideal gas law holds as the equation of state.
31. What are the basic postulates of the transition state theory (TST)?
32. What is the universal frequency of TST equal to?
33. How does the expression for the rate constant derived by TST account for system non-ideality?
34. What is the relationship between the Boltzmann constant and the ideal gas constant?
35. Using TST and Debye-Huckel theory what relation results for the dependence of the rate constant on ionic strength of the solution.
36. What is an elementary reaction? What can one say about stoichiometric coefficients for an elementary reaction?
37. What is the law of mass action? When does it apply?
38. In gas phase reactions bimolecular reactions can occur between what type of species? The rate of bimolecular reactions is of what order?
39. What gas phase trimolecular reactions do you know? What is the overall reaction order?
40. Are gas phase unimolecular reactions always first order?

41. What is the Lindemann – Christensen mechanism?
42. How do we obtain the rate forms for free radical recombination reactions?
43. What are the key differences between gas phase reactions and reactions in solution?
44. What relationship between reaction rate constant and solvent properties does TST predict?
45. What is diffusion?
46. If elementary reactions in solution involve ions or other charged species how does TST account for the effect of the electric field?
47. What dependence of the rate constant on solvent and ion properties is obtained by TST via the dual sphere and single sphere model?
48. What is Ficks First Law of diffusion?
49. What is Ficks Second Law of diffusion?
50. What is the RMS displacement equal to according to the diffusion equation?
51. What is the meaning of a diffusion limited reaction in the liquid state? What is the value of the rate constant for such diffusion limited reaction?
52. What is the expression for the apparent rate constant for a bimolecular liquid phase reaction that is controlled both by kinetics (i.e. transition state complex transformation) and diffusion.

53. What is a reaction mechanism?
54. What is the difference between an “open” and “closed” reaction mechanism sequence?
55. What is the relationship between the stoichiometry of individual mechanistic steps and the overall stoichiometry for mechanisms containing a closed sequence?
56. What are the steps for deriving an overall rate expression in terms of the concentrations of stable species only when applying PSSA to a postulated mechanism?
57. What are the key features in deriving a rate form based on RLSA to a postulated mechanism?
58. What is characteristic reaction time? How does it relate to reaction half life?
59. How is quantum yield defined for photochemical reactions?
60. What is the maximum ozone concentration proportional to if one considers only NO, NO₂, and O₃?
61. What are the NO_x and CO roles in ozone formation? What cyclic catalytic mechanisms do they drive?
62. Where does most of sulfur oxidation occur in the atmosphere, in the gas phase or liquid phase?
63. What are the key reactions in oxidation of S(IV) to S(VI)? Name a few.
64. What are the key five characteristic times for reaction of a gas phase reactant in a liquid droplet?

65. Which of the above characteristic times are most likely to be rate controlling for a:

a) highly soluble gas, b) slightly soluble gas.

66. Write the basic conservation law for a chemical species j in a well mixed single phase system that is:

a) closed, b) open. Identify all the terms.

67. Write the basic conservation law for a chemical species j in a two phase well mixed system that is : a) closed , b) open. Identify all the terms. Do not assume that the system is equilibrated.

68. Modify the equations developed in answering question 67 to the form appropriate when all species are equilibrated between the two phases.

69. Explain the meaning of the modified Henry's constant for a soluble gas that upon dissolution dissociates. Use ammonia as an example.

70. Illustrate the use of equations developed above to treat sulfur dioxide oxidation in air that contains L volume fraction of water in droplets form. Assuming that the only species originally present in the gas phase are nitrogen, oxygen, carbon dioxide, sulfur dioxide, and ozone show which equations would need to be solved to monitor the evolution of pH, $S(VI)$ concentration in the liquid phase. Use information provided in the notes. Do not forget to specify the electroneutrality equation. Assume a closed system.