

THERMODYNAMICS & ELECTROCHEMISTRY SYLLABUS

I. MAIN TOPICS:

Thermodynamics

- A. Spontaneous Processes
- B. Entropy and the Second Law of Thermodynamics
- C. The Molecular Interpretation of Entropy
- D. Entropy Changes in Chemical Reactions
- E. Gibbs Free Energy
- F. Free Energy and Temperature
- G. Free Energy and the Equilibrium Constant

Electrochemistry

- H. Oxidation–Reduction Reactions
- I. Balancing Oxidation–Reduction Reactions
- J. Voltaic/Galvanic Cells
- K. Cell EMF
- L. Spontaneity of RedOx reactions
- M. Effect of Concentration on Cell EMF
- N. Batteries
- O. Corrosion
- P. Electrolysis

II. OBJECTIVES/GUIDELINES:

Thermodynamics

1. How would you define a spontaneous process?
2. Temperature, internal energy and enthalpy are state functions. Remember, state functions are properties that define a state and do not depend on how the system arrives at that state.
3. The First Law of Thermodynamics says $\Delta E = q + w$. ΔE is the change in internal energy. It is the sum of q (the heat absorbed by the system, from the surroundings) and w (the work done on the system by the surroundings).
4. What is the difference between a reversible process and an irreversible one? Be able to relate these processes to the work involved.
5. Whenever a chemical system is in equilibrium, reactants and products can interconvert reversibly.
6. In any spontaneous process, the path between reactants and products is irreversible.
7. Be able to envision two round bottom flasks joined by a closed stopcock. One side has much greater pressure than the other. Try to predict what will happen when the valve is opened. Where will the gas go? Is this process spontaneous? Is it reversible under the same conditions?
8. What is entropy? What symbol is used to represent entropy? What happens to the entropy of the system when it becomes more disordered? Which Thermodynamic Law discusses entropy? What does it say?
9. Be able to distinguish between the system and the surroundings! Are you referring to the entropy of the system, S , or the entropy of the surroundings, S_{UNIV} ?
10. Become familiar with degrees of freedom and the translational/vibrational/rotational motion that occurs in all molecules not at absolute zero. (Which Thermodynamic Law discusses this?)
11. Familiarize yourself with Boltzmann's constant and his important mathematical distributions.
12. The entropy change that takes place in a particular reaction is described by the equation:
$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$
13. Unlike molar enthalpies, molar entropies are given at 298K. They are not zero!
14. The more complex a species (mass, # of atoms) the greater its molar entropy. Physical state can also affect molar entropy quantities (gas is greater than solid).
15. Is it easier to calculate absolute entropy values or changes in entropy values?
16. Gibbs Free Energy describes the energy available to do work.
17. $\Delta G = \Delta H - T\Delta S$. As you can see, Gibbs' F. E. is related to enthalpy, temperature and entropy.

18. If ΔG is negative, the reaction is spontaneous in the forward direction.

If ΔG is zero, the reaction is at equilibrium.

If ΔG is positive, the reaction in the forward direction is nonspontaneous; work must be supplied from the surroundings to make it occur. The reverse reaction will be spontaneous.

19. What are the conditions of standard free energies of formation (ΔG°_f)? How do they differ from those conditions used in the study of thermochemistry (enthalpies of formation ΔH°_f)?

20. Familiarize yourself with the table on page 760. This will help you determine what the outcome of a calculation should be.

21. Discussing entropy and free energy under non-standard conditions involves the inclusion of Q and the rate constant:
 $\Delta G = \Delta G^\circ + RT \ln Q$ What is the difference between ΔG and ΔG° ?

Electrochemistry

22. Oxidation-Reduction reactions and their balancing was covered in the 1st semester's aqueous chemistry unit. Please look back to your notes for specific RedOx information.

23. Intimately associate yourself with a galvanic cell (otherwise known as a voltaic cell). We drew a picture of this in lab. If needed refer to your diagram.

24. What are the cathode and the anode? What processes take place at these locations? Where are the electrons coming from? Where are they going? (Remember, anode and oxidation go together because they both start with vowels!).

25. What is the purpose of the salt bridge? Can you diagram where ions are traveling? What is driving them?

26. Which electrode is losing mass? Which is gaining mass?

27. Where in the system do you incorporate the voltmeter?

28. What does cell EMF stand for? How does this relate to the spontaneity of a RedOx reaction?

29. Familiarize yourself with standard reduction potentials for the half reactions. This is the handout you have been using all along as an activity series. What is the purpose of a SHE?

30. Be able to calculate voltages needed or provided by certain reactions. What if a reaction is not spontaneous? How much voltage is needed to drive this reaction? How does an electrolytic cell differ from a voltaic one?

31. How are Gibbs's Free energy and E (emf) of a cell related?

32. Be able to convert a Faraday into the charge of electrons. Can you see how this is useful in relating chemistry to voltage?

33. Be able to perform calculations using the Nernst equation when non-standard solution concentrations are being used. $E = E^\circ - (RT/nF) \ln Q$

34. Be able to perform calculations pertaining to emf and chemical equilibrium with the following equations:

$$0 = E^\circ - (RT/nF) \ln K_{eq} \quad \text{OR} \quad \log K_{eq} = nE^\circ/0.0592 \quad (T = 298K)$$

35. Relate redox reactions to galvanic corrosion (statue of liberty), electrolysis (Hoffmann apparatus and a Hydrogen economy) and electroplating (chromed bumpers, etc).

Complete the following problems from your Brown, LeMay & Bursten chemistry text. Show all of your work! (No Work = No Credit). The answers to the odd numbered problems are in the back of your text. It is your responsibility to get yourself in an academic position to answer ALL of these problems. If needed – PLEASE ASK ME FOR HELP!

Problem Set # 30 (last one . . .WHOOT!) :

Chapter 19: 1, 4, 7, 30, 38, 40, 65 Chapter 20: 3, 6, 16, 20, 26, 30, 42, 48, 54, 80

Due Date: _____

GOOD LUCK ON THE AP EXAM!!!