CHEM 481. Assignment 0. Review of General Chemistry. Answers

1. **What are the three fundamental particles from which atoms are built? What are their electric charges? Which of these particles constitute the nucleus of an atom? Which is the least massive particle of the three?**
   Proton (+), neutron (no charge) and electron (–). The electron is by far the lightest.

2. **Lithium has two stable isotopes: $^6$Li and $^7$Li. One of them has an abundance of 92.5%, and the other has an abundance of 7.5%. Knowing that the atomic mass of lithium is 6.941, which is the more abundant isotope?**
   Calculate the average based on one assumption: \[
   \frac{7.5}{100} \times 6\text{ amu} + \frac{92.5}{100} \times 7\text{ amu} = 6.93\text{ amu}.
   \]
   This value is close enough, especially when we recognize that the mass of the isotopes is not exactly 6 and 7, though its close. We conclude that $^7$Li is the more abundant form of the element.

3. **What was incorrect about Mendeleev’s original concept of the periodic table? What is the modern ‘law of chemical periodicity,’ and how is this related to Mendeleev’s ideas?**
   Mendeleev organized the sequence of elements based on their atomic mass (the only quantity available to him). Nowadays we organize the elements in terms of their number of protons (the atomic number); in a few cases the sequences differ because of the occurrence of isotope abundances that reverse the mass and number sequence. Such exceptions are rare, however.

4. **What is the difference between a group and a period in the periodic table?**
   The groups are the vertical columns; the periods the horizontal rows. The groups collect elements that have similarities in chemical properties because the rows are repeating sequences of valence electron configurations - the periodicity.

5. **Name and give symbols for (a) three elements that are metals, (b) four elements that are nonmetals, (c) and two elements that are metalloids. In each case locate the element in the periodic table by giving the group and period in which the element is found.**
   Metalloids are: B, Si, Ge, As, Sb, Te; elements to left of the metalloids are metals; those to right are non-metals.

6. **Calcium reacts with air to form a compound in which the ratio of calcium to oxygen atoms is 1:1; that is, the formula is CaO. Based on this fact, predict the formulas for compounds formed between oxygen and the Group 2 elements.**
   We predict: BeO, MgO, CaO, SrO, BaO, RaO.

7. **Compare the formulas of the compounds formed between Cl and Na, Mg, and Al. Can you see a pattern in these formulas? Describe this pattern. Based on this pattern, predict the formula of a compound formed between Si and Cl.**
   Group 1: NaCl; Group 2: MgCl2; Group 13: AlCl3; Group 14: CCl4. Note that for the groups 13 and beyond, the group valence is given by [Group number – 10]. This is easy to remember, and is a small price to pay for a unique label for the 18 element groups of the main and transition elements, for which periodic variation is significant.

8. **The compound $(NH_4)_2CO_3$ consists of two polyatomic ions. What are the names and electric charges of these ions? What is the molar mass of this compound?**
   NH$_4^+$, ammonium. CO$_3^{2–}$, carbonate. Molar mass is about 96.11.

9. **Potassium chloride, KCl, melts at 771°C. In contrast, magnesium oxide, MgO, melts at 2826°C. Using Coulomb’s law, suggest a reason for the great difference in the melting points of KCl and MgO.**
   Both are salts, but its $K^+…\text{Cl}^–$ versus Mg$^{2+}…\text{O}^{2–}$. The Coulombs law $F = \frac{|q_1| \times |q_2|}{r^2}$ would therefore give a fourfold greater force for MgO than in KCl, so a higher melting point for the solid is not unexpected.

10. **Name each of the each of the following ionic compounds, and give the formula, charge, and number of each ion that makes up the compound:**
    - (a) Ca(CH$_3$CO$_2$)$_2$ calcium acetate $\text{Ca}^{2+}$ CH$_3$CO$_2^–$
    - (b) Co$_3$(SO$_4$)$_2$(OH)$_2$ cobalt(III) sulfate $\text{Co}^{3+}$ $\text{SO}_4^{2–}$ $\text{OH}^-$
    - (c) Al(OH)$_3$ aluminum hydroxide $\text{Al}^{3+}$ $\text{OH}^–$
    - (d) KH$_2$PO$_4$ potassium dihydrogen phosphate $\text{K}^+$ $\text{H}_2\text{PO}_4^–$
    - (e) CuCO$_3$ copper carbonate $\text{Cu}^{2+}$ $\text{CO}_3^{2–}$
11. If the hydrated compound \( \text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \) is heated gently, the water of hydration is lost. If you have 0.865 g of the hydrated compound and obtain 0.679 g of \( \text{UO}_2(\text{NO}_3)_2 \) on heating, how many molecules of water of hydration were in each formula unit of the original compound?

\[
\frac{0.186 \text{ g H}_2\text{O}}{18.02 \text{ g/mol}} = 0.013 \text{ mol H}_2\text{O} \quad \frac{0.679 \text{ g UO}_2(\text{NO}_3)_2}{394.0 \text{ g/mol}} = 0.00172 \text{ mol UO}_2(\text{NO}_3)_2
\]

This is the ratio 0.013/0.00172 = 6/1; hence the formula of the hydrated compound: \( \text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \)

12. What substances in the following list are common oxidizing or reducing agents: \( \text{HNO}_3 \), \( \text{Na} \), \( \text{NaCl} \), \( \text{O}_2 \), \( \text{CrCl}_3 \), and \( \text{KMnO}_4 \)? Identify each such substance as an oxidizing or reducing agent.

Oxidizing agents: \( \text{HNO}_3 \), \( \text{O}_2 \), \( \text{CrCl}_3 \), and \( \text{KMnO}_4 \)
Reducing agent: \( \text{Na} \)
Neither: \( \text{NaCl} \)

13. Balance the following equations:

(a) Reaction to produce ‘superphosphate’ fertilizer:
\[ \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 2 \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Ca(H}_2\text{PO}_4)_2(\text{aq}) + 2 \text{CaSO}_4(\text{s}) \]

(b) Reaction to produce diborane, \( \text{B}_2\text{H}_6 \):
\[ 2 \text{NaBH}_4(\text{s}) + 2 \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{B}_2\text{H}_6(\text{g}) + 2 \text{H}_2(\text{g}) + \text{Na}_2\text{SO}_4(\text{aq}) \]

(c) Reaction to produce tungsten metal from tungsten(VI) oxide:
\[ \text{WO}_3(\text{s}) + 3 \text{H}_2(\text{g}) \rightarrow \text{W}(\text{s}) + 3 \text{H}_2\text{O}(\text{l}) \]

14. (a) Write a balanced equation for reaction of the basic oxide, magnesium oxide, with water.

\[ \text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \]

(b) Write a balanced equation for the reaction of sulfur trioxide with water.

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]

15. Mg metal reacts readily with \( \text{HNO}_3 \), and the following compounds are all involved:

\[ \text{Mg(s)} + \text{HNO}_3(\text{aq}) \rightarrow \text{Mg(NO}_3)_2(\text{aq}) + \text{NO}_2(\text{g}) + \text{H}_2\text{O(l)} \]

(a) Balance the equation for the reaction.
(b) Name each compound.
(c) Write the net ionic equation for the reaction.
(d) What type of reaction is this?

\[ \text{Mg(s)} + 4 \text{H}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{NO}_2(\text{g}) + 2 \text{H}_2\text{O(l)} \]

This is a redox reaction.

16. Calculate the enthalpy change, \( \Delta H^\circ \), for the formation of 1 mol of strontium carbonate (the material that gives the red color in fireworks) from its elements:

\[ \text{Sr(s)} + \text{C(graphite)} + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{SrCO}_3(\text{s}) \]

The experimental information available is:

\[ \text{Sr(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{SrO}(\text{s}) \quad \Delta H^\circ_{\text{rxn}} = -592 \text{ kJ} \]
\[ \text{SrO}(\text{s}) + \frac{1}{2} \text{CO}_2(\text{g}) \rightarrow \text{SrCO}_3(\text{s}) \quad \Delta H^\circ_{\text{rxn}} = -234 \text{ kJ} \]
\[ \text{C(graphite)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ_{\text{rxn}} = -394 \text{ kJ} \]
\[ \text{Sr(s)} + \text{C(graphite)} + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{SrCO}_3(\text{s}) \quad \Delta H^\circ_{\text{rxn}} = -1220 \text{ kJ} \]
18. Give the equation for each of the following important mathematical relations:

(a) The relationship between wavelength, frequency, and velocity of radiation \[ \lambda = \frac{c}{\nu} \]

(b) The relation between energy and frequency of radiation \[ E = h\nu \]

(c) The energy of an electron in a given energy state of the H atom \[ \Delta E = E_{\text{final}} - E_{\text{initial}} = R\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \]

19. State Planck’s equation in words and as a mathematical relation.

Equation is 18(c). The energy of a photon of electromagnetic radiation is given by the product of the frequency multiplied by \( h \), Planck's constant. Thus electromagnetic radiation is quantized, i.e. its energy is a multiple of finite energy units.

20. Name the colors of visible light beginning with that of highest energy.

Violet, Indigo, Blue, Green, Yellow, Orange, Red

21. Draw a picture of a standing wave, and use this to define the terms wavelength, amplitude, and node.

Wavelength is the length of the repeating units (three are visible); the peak-to-peak distance of the wave
Amplitude: the maximum height/depth of the wave; the amplitude can be increased without changing the wavelength
Node: a point in a standing wave that has zero amplitude but is not at either end; this wave has three nodes

22. Which of the following best describes the importance of the photoelectric effect as explained by Einstein?

(a) Light is electromagnetic radiation.
(b) The intensity of a light beam is related to its frequency.
(c) Light can be thought of as consisting of massless particles whose energy is given by Planck’s equation, \( E = h\nu \)

23. What is a photon? Explain how the photoelectric effect implies the existence of photons.

A photon expresses the energy of a wave-packet, \( h\nu \), the smallest energy unit for a given electromagnetic wave. If the energy of the wavepacket is as large as or larger than the binding energy of the metal, an electron is ejected; the kinetic energy of the ejected electron reflects the difference between the binding energy and \( h\nu \). However, if the energy is too small, no electrons can be ejected, and the current flow remains zero.

24. What are two major assumptions of Bohr’s theory of atomic structure?

Bohr (1) assumed that electrons in atoms are quantized, and (2) that they will remain in their lowest energy state unless acted upon by an outside source of energy.

25. In what region of the electromagnetic spectrum is the Lyman series of lines found? The Balmer series?

Lyman series is in the ultra-violet (higher energy); Balmer is in the visible (lower energy)

26. Light is given off by a sodium- or mercury-containing street-light when the atoms are excited in some way. The light you see arises for which of the following reasons:

(a) Electrons moving from a given energy level to one of higher \( n \)
(b) Electrons being removed from the atom, thereby creating a metal cation
(c) Electrons moving from a given energy level to one of lower \( n \)
(d) Electrons whizzing about the nucleus in an absolute frenzy
27. What is Heisenberg’s uncertainty principle? Explain how it applies to our modern view of atomic structure.
Heisenberg concluded that it was impossible to fix both the position of an electron in an atom and its energy with any degree of certainty. One way to understand this principle is that the electron is so small that any attempt to probe its location will inevitably disturb its position. The probe will return information regarding where the electron was, but it will no longer be there. This idea feeds directly into our modern understanding that we can only describe the probability of finding any electron of a given energy within a region of space around the nucleus of the atom.

28. How do we interpret the physical meaning of the square of the wave function? What are the dimensions of \( \psi^2 \)?
The square of the wave function reports the electron density at any given point around the nucleus. It has the dimensions of 1/volume.

29. What are the three quantum numbers used to describe an orbital? What property of an orbital is described by each quantum number? Specify the rules that govern the values of each quantum number.
Principal quantum number, \( n \), gives the relative size of the orbital; angular momentum quantum number, \( l \), gives the shape of the orbital; magnetic quantum number, \( m_l \), gives the relative orientation of the orbitals in space.

30. On what does the amplitude of the electron wave in an atom depend?
The amplitude depends on a number of factors: the values of the quantum numbers, the distance from the nucleus, the shape of the orbital, and in particular, the location of the nodal planes and nodal surfaces where the amplitude is zero.

31. Give the number of planar nodes for each orbital type: \( s \), \( p \), \( d \), and \( f \).
The number of planar nodes is given by the \( l \) quantum number: 0 for \( s \), 1 for \( p \), 2 for \( d \) and 3 for \( f \).

32. What is the maximum number of \( s \) orbitals found in a given electron shell? The maximum number of \( p \) orbitals? Of \( d \) orbitals? Of \( f \) orbitals?
Within a given value of \( n \) (a shell), there are one \( s \), three \( p \), five \( d \) and seven \( f \) orbitals (the multiplicity of \( m_l \)).

33. Match the values of \( l \) shown in the table with orbital type (\( s \), \( p \), \( d \), or \( f \)):
   \[
   \begin{array}{|c|c|}
   \hline
   l & \text{Orbital Type} \\
   \hline
   3 & f \\
   0 & s \\
   1 & p \\
   2 & d \\
   \hline
   \end{array}
   \]

34. Sketch a picture of the 90% boundary surface of an \( s \) orbital and the \( px \) orbital. Be sure the latter drawing shows why the \( p \) orbital is labeled \( px \) and not \( py \), for example.

35. Answer the following questions:
   (a) When \( n = 4 \), \( l = 2 \), and \( m_l = -1 \), to what orbital type does this refer? (Give the orbital label, such as 1s.) a 4d orbital
   (b) How many orbitals occur in the \( n = 5 \) electron shell? How many subshells? What are the letter labels of the subshells?
      1 \( s \), 3 \( p \), 5 \( d \), 7 \( f \), 9 \( g \) orbitals, or 25 orbitals in the \( n = 5 \) shell (note that this is just \( 5^2 = 25 \) orbitals, a general rule!)
   (c) If a subshell is labeled \( g \), how many orbitals occur in the subshell? What are the values of \( m_l \)?
      There are 9 orbitals in a \( g \) subshell, with \( m_l = 0, \pm 1, \pm 2, \pm 3 \), and \( \pm 4 \)
36. Which of the following represent valid sets of quantum numbers? For a set that is invalid, explain briefly why it is not correct.
   (a) \( n = 3, l = 3, m_l = 0 \) Not valid, since maximum \( l \) is \( n - 1 \).
   (b) \( n = 2, l = 1, m_l = 0 \) Valid (2p)
   (c) \( n = 6, l = 5, m_l = -1 \) Valid (6h)
   (d) \( n = 4, l = 3, m_l = -4 \) Not valid, since minimum \( m_l \) is \(-l\).

37. If sufficient energy is absorbed by an atom, an electron can be lost by the atom and a positive ion formed. The amount of energy required is called the ionization energy. In the \( H \) atom, the ionization energy is that required to change the electron from \( n = 1 \) to \( n = \infty \). Calculate the ionization energy for \( \text{He}^+ \) ions. Is the ionization energy of \( \text{He}^+ \) more or less than that of \( H \)? (Bohr’s theory applies to \( \text{He}^+ \) because it, like the \( H \) atom, has a single electron. However, the electron energy is now given by \( E = -Z^2 \frac{R \hbar c}{n^2} \), where \( Z \) is the atomic number of helium.)

\[
E = \frac{- (2)^2 \times 1.097 \times 10^7 \text{m}^{-1} \times 6.626 \times 10^{-34} \text{Js} \times 2.998 \times 10^8 \text{m/s}}{1^2} = -8.717 \times 10^{-18} \text{ J/ion} \text{ or } -5249 \text{kJ/mol}
\]

Thus the ionization energy of \( \text{He}^+ \) is four times as large as that of hydrogen, because of the greater nuclear charge in He.

38. Give the four quantum numbers, specify their allowed values, and tell what property of the electron they describe.
   - Principal quantum number \( n \) = 1, 2, 3, ...., \( \infty \) relative size of the orbital
   - Angular momentum quantum number \( l \) = 0, 1, 2, ...., \( (n-1) \) shape of the orbital
   - Magnetic quantum number \( m_l \) = 0, \( \pm 1 \), \( \pm 2 \), ...., \( \pm l \) relative orientation of the orbitals
   - Electron spin quantum number \( m_s \) = \( +\frac{1}{2} \) or \( -\frac{1}{2} \) relative spin of electron (up or down)

39. What is the Pauli exclusion principle?
   States that no two electrons on a single atom (or molecule) may have all four quantum numbers the same. This creates the capacity of two electrons per orbital, provided that they have opposing electron spin (spin-pairing).

40. Using lithium as an example, show the two methods of depicting electron configurations (orbital box diagram and spectroscopic notation).

   Spectroscopic notation: \( 1s^22s^1 \)
   Box notation: \[
   \begin{array}{ccc}
   \text{\textcircled{1}} & \text{\textcircled{2}} & \text{\textcircled{3}} \\
   \end{array}
   \]

41. What is Hund’s rule? Give an example of its use.
   Hund’s rule of maximum multiplicity states that for any degenerate levels, the electrons must fill different orbitals with the same spin before spin pairing within the same orbital. Thus the configuration of \( N \) is: \( 1s^22s^22p_x^22p_y^12p_z^1 \) and not \( 1s^22s^22p_x^22p_y^2 \).

42. What is the noble gas notation? Write an electron configuration using this notation.
   This notation shortens the configuration to the valance electrons since the last complete noble gas. Thus the element sodium is abbreviated to: \([\text{Ne}]3s^1\) rather than the full \( 1s^22s^22p^63s^1 \). We will always use this short notation, but know the \([\text{NG}]\)!

43. Name an element of Group 13. What does the group designation tell you about the electron configuration of the element?
   Boron, aluminum, gallium, indium or thallium. All have the \( ns^2np^1 \) valence electron configuration.

44. Name an element of Group 6. What does the group designation tell you about the electron configuration of the element?
   Chromium, molybdenum, tungsten or seaborgium. All have the \( ns^2(n-1)d^{10} \) or \( ns^1(n-1)d^{10} \) valence electron configurations.

45. What element is located in the fourth period of Group 14? What does the element’s location tell you about its electron configuration?
   Germanium, with the \( 4s^23d^{10}4p^2 \) valence electron configuration (after an Ar core).

46. What element is located in the fifth period of Group 5? What does the element’s location tell you about its electron configuration?
   Niobium, with the \( 5s^24d^3 \)

47. Tell what happens to atomic size, ionization energy, and electron affinity when proceeding across a period and down a group.
   Across a period: size decreases; ionization energy increases, and electron affinity increases
Down a group: size increases; ionization energy decreases, and electron affinity decreases.

48. Explain briefly why each of the following is not a possible set of quantum numbers for an electron in a silicon atom (in its ground state). In each case, change the incorrect value (or values) in some way to make the set valid.
   (a) \( n = 4, \ l = 2, \ m_l = 0, \ m_s = 0 \quad m_s \) must be \( \pm \frac{1}{2} \) also there is no 4d or 3d level in silicon; try 3,1,0,1/2
   (b) \( n = 3, \ l = 1, \ m_l = -3, \ m_s = -\frac{1}{2} \quad 3p \) is possible, but then \( m_l \) must be 0 or \( \pm 1 \).
   (c) \( n = 3, \ l = 2, \ m_l = -1, \ m_s = +\frac{1}{2} \quad 3d \) is not possible; try \( l = 1 \) again.

49. Arrange the following elements in order of increasing size: Ca, Rb, P, Ge, and Sr. \( P < Ge < Ca < Rb \)

50. Select the atom or ion in each pair that has the larger radius.
   (a) Cs or Rb Cs (directly below Rb in the periodic table)
   (b) \( O^+ \) or \( O \) \( O^2 \) because the same 6 protons now attract 8 rather than 6 valence electrons in the same shell
   (c) Br or As As, since size decreases from left to right.

51. Arrange the following atoms in the order of increasing ionization energy: F, Al, P, and Mg. \( Mg < Al < P < F \)

52. Periodic trends. Explain each answer briefly.
   (a) Rank the following in order of increasing atomic radius: O, S, and F. F < O < S; size incr. down, decr. across.
   (b) Which has the largest ionization energy: P, Si, S, or Se? S; IE incr. up and across the PT.
   (c) Place the following in order of increasing radius: Ne, \( O^2 \), \( N^2 \), F. Ne < F < \( O^2 < N^2 \), isoelectronic, but less protons
   (d) Place the following in order of increasing ionization energy: Cs, Sr, Ba. Cs < Ba < Sr; IE incr. up and across the PT

53. Define bond dissociation energy. Does the enthalpy change for a bond-breaking reaction [such as \( H–Cl(g) \rightarrow H(g) + Cl(g) \)] always have a positive sign, always have a negative sign, or may the sign vary? Explain briefly.
   The energy required to break one mole of bonds and separate the fragments far apart in the gas phase. It is always an endothermic process, since bonds form by releasing energy, so it costs energy to break them.

54. What is the relationship between bond order, bond length, and bond energy for a series of related bonds, say carbon-nitrogen bonds?
   Higher bond order has higher bond energy and shorter bond length.

55. If you wished to calculate the enthalpy change for the reaction
   \[ O=O(g) + 2 \text{H–H(g)} \rightarrow 2 \text{H–O–H(g)} \]
   what bond energies do you need? Outline the calculation, being careful to show correct algebraic signs.
   Break one O=O double bond and two H–H bonds (+ve signs); form 4 H–O single bonds (-ve signs).

56. Describe the trends in electronegativity in the periodic table.
   Electronegativity increases from left to right and from bottom to top across the PT; Fr is the lowest, F (or He) the highest.

57. Describe the difference between the oxidation number of an atom and its formal charge. Which is often the more realistic description of the charge on an atom in a molecule?
   A good example is the \( \text{SO}_4^{2-} \) ion, in which the sulfur is in the +6 oxidation state, but has a 2+ formal charge in the Lewis structure. 2+ is actually close to the calculated positive charge at sulfur in this molecule.

58. What is the principle of electroneutrality? How does this apply to the possible resonance structures of \( \text{CO}_2 \)?
   Atoms in molecules (or ions) should have formal charges as small as possible. In O=C=O, the most important resonance structure has no formal charges, while the O–C=O and O=C–O structures do have charge, and are thus much less important.

59. What is the VSEPR theory? What is the physical basis of the theory?
   If we assume that electrons around atoms occupy hybrid orbitals, i.e. act as discrete electron pairs, then the VSEPR theory minimizes the electrostatic electron-electron repulsion by separating the pairs from each other in space as far as possible.

60. What is the difference between the electron-pair geometry and the molecular geometry of a molecule? Use the water molecule as an example in your discussion.
   The electron pair geometry of water is tetrahedral (four electron pairs around O, pointing in the octahedral direction. But since two are lone pairs, the molecular geometry of water is best described as bent (but with a 104° bond angle).
61. Designate the electron-pair geometry for each case of two to six electron pairs around a central atom.

62. Draw a trigonal bipyramid of electron pairs. Designate the axial and equatorial pairs. Do axial and equatorial pairs also occur in an octahedron?  Trigonal bipyramidal: The octahedral shape has no ax/eq distinction.

63. Does ammonia, NH₃, have a dipole moment?  If so, what is the direction of the net dipole in NH₃?
   Yes, ammonia is polar, with a dipole moment pointing along the three-fold axis through the nitrogen atom, and directed toward the nitrogen and away from the hydrogens.

64. Draw Lewis structures for the following molecules or ions:
   (a) NF₃  (c) HOB₃  (b) ClO₃⁻  (d) SO₃²⁻  (e) NO₂⁺  (f) PO₄³⁻

65. Show all possible resonance structures for each molecule or ion.
   (a) Nitrate ion, NO₃⁻  (b) Dinitrogen oxide (laughing gas), NNO

66. Chlorine trifluoride, ClF₃, is one of the most reactive compounds known. It reacts violently with many substances generally thought to be inert and was used in incendiary bombs in World War II. It can be made by heating Cl₂ and F₂ in a closed container.
   (a) Write a balanced equation to depict the reaction of Cl₂ and F₂ to give ClF₃.
      Cl₂ + 3 F₂ → 2 ClF₃
   (b) Draw the electron dot structure of ClF₃.
   (c) What is the electron-pair geometry for ClF₃?

   (d) Knowing that the molecule is polar, what can you conclude about the molecular geometry?  Does this establish the geometry unambiguously?
      The polarity is consistent with several AX₃ geometries, e.g. triangular pyramidal and "T"-shaped. It is not consistent with triangular planar however. Thus the polarity of the molecule shows us that of the five electron pairs in a trigonal-bipyramidal arrangement around the Cl atom, two of the equatorial sites must be where the lone pairs are located. The molecule is thus "T" shaped.
   (e) Calculate the standard enthalpy of formation of gaseous ClF₃ using bond energies.
      Bonds broken:
      3 mol F–F = 3 mol × 159 kJ/mol = 477 kJ
      1 mol Cl–Cl = 1 mol × 243 kJ/mol = 243 kJ
      Energy input = 720 kJ
      Bonds formed:
      6 mol Cl–F = 6 mol × 255 kJ/mol = 1530 kJ (Energy released)
\[ \Delta H_{\text{rxn}} = 720 - 1530 = -810 \text{ kJ}; \text{ therefore the enthalpy change per mole of ClF}_3 \text{ is } -405 \text{ kJ} \]

67. Using the rate equation \( \text{Rate} = k[A]^2[B] \), define the order of the reaction with respect to \( A \) and \( B \) and the total order of the reaction.

Second order with respect to [A], first order w.r.t. [B], overall third order reaction.

68. Write the equation that allows us to find the concentration of reactant as a function of time for a first-order reaction. Define each term in the equation.

\[
\ln \left( \frac{[R]_t}{[R]_0} \right) = -kt \quad \text{where} \quad [R]_t \text{ is the concentration at time } t, \quad [R]_0 \text{ is the initial concentration, } t \text{ is time, } k \text{ is a constant}
\]

69. Draw a reaction energy diagram for a one-step exothermic process. Mark the activation energies of the forward and reverse processes and describe how you can calculate the net energy change for the reaction.

The diagram is drawn for an exothermic reaction, with the activation energy for the forward reaction indicated, as well as the net energy released by the reaction. The activation barrier for the reverse (endothermic) reaction equals the sum of the indicated activation barrier and the enthalpy change.

70. The substitution of CO in Ni(CO)\(_4\) was studied some years ago (in the non-aqueous solvents toluene and hexane) and led to an understanding of some of the general principles that govern the chemistry of compounds having metal–CO bonds. (See J. P. Day, F. Basolo, and R. G. Pearson: Journal of the American Chemical Society, Vol. 90, p. 6927, 1968.)

\[
\text{Ni} \quad \text{OC} \quad \text{CO} \quad \text{CO} \quad \text{Ni} \quad \text{OC} \quad \text{CO} \quad \text{L} \quad \text{L} \quad \text{CO} \quad \text{CO} \quad \text{Ni} \quad \text{OC} \quad \text{CO} \quad \text{L} \quad \text{CO}
\]

L in this reaction is an electron-pair donor, like CO, but the atom bearing the pair of electrons to be donated is usually P, as in \( P(CH_3)_3 \). A detailed study of the kinetics of the reaction led to the following mechanism:

- **Slow**: \( \text{Ni(CO)}_4 \rightarrow \text{Ni(CO)}_3 + \text{CO} \)
- **Fast**: \( \text{Ni(CO)}_3 + \text{L} \rightarrow \text{Ni(CO)}_3\text{L} \)

(a) What is the molecularity of each of the elementary reactions?  Slow step unimolecular; fast step bimolecular.

(b) It was found that doubling the concentration of \( \text{Ni(CO)}_4 \) increased the reaction rate by a factor of 2.  Doubling the concentration of \( L \) had no effect on the reaction rate. Based on this information, write the rate equation for the reaction. Does this agree with the mechanism above?

This implies the rate law: \( \text{Rate} = k[\text{Ni(CO)}_4] \), which certainly fits the slow step of the mechanism.

(c) The experimental rate constant for the reaction, when \( L = P(CH_3)_3 \), is \( 9.3 \times 10^{-3} \text{ s}^{-1} \) at 20°C.  If the initial concentration of \( \text{Ni(CO)}_4 \) is 0.025 M, what is the concentration of the product after 5.0 min?

\[
\ln \frac{x}{0.025} = -(9.3 \times 10^{-3} / \text{s})(5.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}})
\]

\[ x = 0.00153 \]

71. Name three important features of the equilibrium condition.

Chemical reactions are reversible; equilibria are dynamic; and the nature of the equilibrium state is the same, no matter what the direction of approach

72. Decide if each of the following statements is true or false. If false, change the wording to make it true.

(a) The magnitude of the equilibrium constant is always independent of temperature.  **True**
(b) When two chemical equations are added to give a net equation, the equilibrium constant for the net equation is the product of the equilibrium constants of the summed equations.  **True**
(c) The equilibrium constant for a reaction has the **same** inverse value as \( K \) for its reverse.  **False**
(d) Only the concentration of \( \text{CO}_2 \) appears in the equilibrium constant expression for the reaction: \( \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \).  **True**
(e) For the reaction: \( \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \), the value of \( K \) is the same whether the amount of \( \text{CO}_2 \) is expressed in moles per liter or as gas pressure.  **False**
73. Write equilibrium constant expressions \((K_p)\) for the following reactions.

(a) \(2 \text{H}_2\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) + \text{O}_2(g)\) \(K = [\text{H}_2\text{O}][\text{O}_2] / [\text{H}_2\text{O}_2]^2\)

(b) \(\text{PCl}_3(g) + \text{Cl}_2(g) \rightarrow \text{PCl}_5(g)\) \(K = [\text{PCl}_5] / [\text{PCl}_3][\text{Cl}_2]\)

74. Outline the main ideas of the Arrhenius, Brønsted, and Lewis theories of acids and bases. How does the Lewis theory relate to the Brønsted theory?

- **Arrhenius:** an acid HA is a species that dissociates in solution as a source of \(\text{H}^+\)
- **Brønsted:** an acid HA reacts with a base B to transfer a proton to the B; a base B is a proton acceptor towards the acid HA; the products HB\(^+\) and A\(^-\) are known as the conjugate acid and conjugate base, respectively
- **Lewis:** a Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor. We can re-write the Brønsted reaction and describe it as the displacement of the base A\(^-\) by the base B at the acid H\(^+\). This is how the two theories are related.

75. Write a balanced equation depicting the autoionization of water. What is the experimental evidence for this reaction?

\[2 \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-\] The evidence is the (weak) conductivity of pure water and the pH of 7.0.

76. Write balanced chemical equations showing that phosphoric acid is a polyprotic acid.

1. \(\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+\)
2. \(\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+\)
3. \(\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{PO}_4^{3-} + \text{H}_3\text{O}^+\)

77. Write balanced chemical equations showing that the hydrogen sulfate ion, \(\text{HSO}_4^-\), is an amphiprotic substance.

1. \(\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+\)
2. \(\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_4 + \text{OH}^-\)

78. Designate the Brønsted acid and the base on the left side of each of the following equations, and designate the conjugate partner of each on the right side:

- \(\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+ (\text{aq}) + \text{NO}_2^- (\text{aq})\)
- \(\text{NH}_4^+ (\text{aq}) + \text{CN}^- (\text{aq}) \rightarrow \text{NH}_3(\text{aq}) + \text{HCN}(\text{aq})\)

79. Show that water can be a Brønsted base and a Lewis base.

- When water accepts a proton from an acid, forming \(\text{H}_3\text{O}^+\), it acts as a Brønsted base;
- When water adds via its lone pair to a metal ion, to give for example \([\text{Fe(OH}_2\text{)}_6]^{2+}\), it acts as a pure Lewis base to the Lewis acid \(\text{Fe}^{2+}\).

80. Explain the terms ‘saturated,’ ‘not saturated’ (or ‘under-saturated’), and ‘supersaturated.’ Use an equilibrium such as \(\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{F}^- (\text{aq})\) to illustrate your answer.

If there is solid \(\text{CaF}_2\) in the mixture in equilibrium with dissolved calcium and fluoride ions, the system is at equilibrium and saturated. If there is no solid calcium fluoride and the system is at equilibrium, then the solution is under-saturated. If the calcium and fluoride ion concentrations are greater than that at which precipitate should form from the solubility product (the equilibrium constant), then the solution is supersaturated and unstable; disturbances tend to induce precipitation until a saturated solution occurs.

81. What is the common ion effect? Use the equilibrium \(\text{Fe(OH)}_2(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + 2 \text{OH}^- (\text{aq})\) in your discussion.

If to a solution saturated in \(\text{Fe(II)}\) and hydroxide ions, in equilibrium with solid iron(II) hydroxide we add either excess iron or hydroxide ions, then the amount of solid will be increased. This is just one example of an application of LeChaterlier's principle.

82. Solid gold(I) chloride, \(\text{AuCl}\), is dissolved when excess cyanide ion, \(\text{CN}^-\), is added to give a water-soluble complex ion. \(\text{AuCl}(\text{s}) + 2 \text{CN}^- (\text{aq}) \rightarrow \text{Au(CN)}_2^- (\text{aq}) + \text{Cl}^- (\text{aq})\)

Show that this equation is the sum of two other equations, one for dissolving \(\text{AuCl}\) to give its ions and the other for the formation of the \(\text{Au(CN)}_2^-\) ion from \(\text{Au}^+\) and \(\text{CN}^-\).

\[\text{AuCl}(\text{s}) \rightarrow \text{Au}^+(\text{aq}) + \text{Cl}^- (\text{aq})\]
\[\text{Au}^+(\text{aq}) + 2 \text{CN}^- (\text{aq}) \rightarrow \text{Au(CN)}_2^- (\text{aq})\]

83. What is meant by a ‘product-favored chemical reaction?’ A reaction for which the equilibrium lies over to the products, identified by a negative sign for the Gibbs free energy of reaction.

84. Criticize the following statements:

(a) The entropy increases in all product-favored reactions. Not true; the entropy may decrease so long as the decrease in enthalpy at the temperature of the reaction overrides this effect.

(b) A reaction with a negative free energy change \((\Delta G^\circ_{\text{rxn}} < 0)\) is predicted to be product-favored with rapid transformation.
of reactants to products. Not true. Thermodynamics never predicts the rate at which reactions may occur.

(c) All product-favored processes are exothermic. Not true. An endothermic reaction may be product-favored if the increase in entropy at that temperature is enough to override the increase in enthalpy.

(d) Endothermic reactions are never product-favored. Not true - see (c).

85. Decide if each of the following statements is true or false. If false, rewrite to make it true.
(a) The entropy of a substance increases on going from the liquid to the vapor state at any temperature. TRUE
(b) An exothermic reaction is always usually product-favored. FALSE
(c) Reactions with a positive $\Delta G^\circ$ and a positive $\Delta S^\circ$ can never be product-favored. TRUE
(d) Reactions with $\Delta G^\circ < 0$ have an equilibrium constant greater than 1. TRUE
(e) When the equilibrium constant of a reaction is less than 1, then $\Delta G^\circ$ is less than 0. FALSE

86. Explain why the entropy of the system increases on dissolving solid NaCl in water. $S^\circ[NaCl(s)] = 72.1 \text{ J/K} \cdot \text{mol}$ and $S^\circ[NaCl(aq)] = 115.5 \text{ J/K} \cdot \text{mol}$. The pure water has a significant degree of organizational order. The dissolving sodium and chloride ions disrupt this structure, so that in fact the entropy of the system increases. Furthermore, the ions are becoming free-floating, rather than being organized in the crystalline NaCl lattice, so their state of disorder is also increase on dissolving.

87. For each of the following processes, give the algebraic sign of $\Delta H^\circ$, $\Delta S^\circ$, and $\Delta G^\circ$. No calculations are necessary; use your common sense.
(a) The splitting of liquid water to give gaseous oxygen and hydrogen, a process that requires a considerable amount of energy. $\Delta H^\circ$ pos, $\Delta S^\circ$ pos, and $\Delta G^\circ$ pos (clearly a non-spontaneous process that requires a lot of energy input to proceed, but entropy does favor this reaction as three molecules of gas are produced from each two molecules of liquid used)
(b) The explosion of dynamite, a mixture of nitroglycerin, $C_3H_5N_3O_9$, and diatomaceous earth, gives gaseous products, such as water, CO$_2$, and others; much heat is evolved. $\Delta H^\circ$ neg, $\Delta S^\circ$ pos, and $\Delta G^\circ$ neg (favoured by enthalpy and entropy)
(c) The combustion of gasoline in the engine of your car, as exemplified by the combustion of octane.

\[ 2\text{C}_8\text{H}_{18}(g) + 25\text{O}_2(g) \rightarrow 16\text{CO}_2(g) + 18\text{H}_2\text{O}(g) \]
$\Delta H^\circ$ neg, $\Delta S^\circ$ pos, and $\Delta G^\circ$ neg (favoured by enthalpy and entropy)

88. In each of the following reactions, identify the substance oxidized and the substance reduced. Identify the oxidizing agent and the reducing agent.
(a) $2\text{Al}(s) + 3\text{Cl}_2(g) \rightarrow 2\text{AlCl}_3(s)$
(b) $\text{FeS}(s) + 3\text{NO}_3^-(aq) + 4\text{H}_3\text{O}^+(aq) \rightarrow \text{NO}(g) + \text{SO}_4^{2-}(aq) + \text{Fe}^{3+}(aq) + 6\text{H}_2\text{O}(l)$

89. Explain the function of a salt bridge in an electrochemical cell.
If we want to get a very accurate voltage under thermodynamic standard conditions in a voltaic cell, then we cannot afford to have any mixing between the two half cells at the cell junction. A well-designed salt bridge can act as a barrier to prevent diffusion of ions between the two half-cells, but not perturb the voltage. The bridge has to have a high conductivity (high concentrations of non-reactive ions to the system being linked).

90. Decide if each of the following statements is true or false. If false, rewrite it to make it a correct statement.
(a) Oxidation always occurs at the anode of an electrochemical cell. TRUE
(b) The anode of a battery is the site of reduction - OXIDATION and is negative.
(c) The potential of a cell does not change with temperature.
(d) All product-favored oxidation-reduction reactions have negative POSITIVE $E^\circ_{net}$

91. Decide which phrase (a through d) best completes the sentence. A product-favored oxidation-reduction reaction has
(a) A positive $\Delta G^\circ$ and a positive $E^\circ$
(b) A negative $\Delta G^\circ$ and a positive $E^\circ$
(c) A positive $\Delta G^\circ$ and a negative $E^\circ$
(d) A negative $\Delta G^\circ$ and a negative $E^\circ$
92. **What are the advantages and disadvantages of lead storage batteries?** Advantages: cheap to manufacture; high charge-densities leading to high initial current; excellent charge-discharge cycling and long life; fairly steady voltage through discharge cycle. Disadvantages: heavy; toxic lead, disposal problem; corrosive electrolyte, sulfuric acid; slow-charging.

93. **How does a fuel cell differ from a battery?** In a fuel cell, an electrochemical reaction occurs that consumes reactants that can be fed into the cell to sustain the reaction. It is thus a direct way to "burn" fuels at low temperature to provide electrical energy, and is thermodynamically very efficient.

94. **Explain why the products of electrolysis of molten NaCl differ from those obtained from aqueous NaCl.** In pure molten NaCl, the reduction product is sodium metal. In an aqueous cell, sodium produces would react directly with the water to give hydrogen and sodium hydroxide. So the first cell produces elemental sodium, the second NaOH and H₂.

95. **Describe the electrochemical method for the manufacture of Cl₂ and NaOH.** By the electrolysis of concentrated salt solutions (brine) at low temperature and with immediate removal of chlorine gas from the reaction mixture (see 94).

96. **What is the difference between anodic and cathodic protection against corrosion? Explain how each works.** Anodic protection involves coating the metal with a layer of stable metal oxide (of the same or a different element) which acts as an impermeable membrane to prevent further oxidation. Cathodic protection involves the sacrificial oxidation of a piece of more reactive metal that is intentionally placed in electrical contact with the protected metal to protect it.

97. **Consult a table of standard redox potentials, and decide which phrase (a through c) best completes the sentence.**

   Zn(s) can:
   (a) Oxidize Fe(s) and Cd(s)
   (b) Reduce Al³⁺ and Mg²⁺
   (c) Reduce Cd²⁺ and Ag⁺

98. **Decide if each of the following statements is true or false. If false, rewrite it to make it a correct statement.**
   (a) The value of an electrode potential **doubles STAYS THE SAME** when the half-reaction is multiplied by a factor of 2. That is, E° for (2 Li⁺ + 2 e⁻ → 2 Li) is twice that for (Li⁺ + e⁻ → Li).
   (b) The equilibrium constant for an oxidation-reduction reaction can be calculated using the Nernst equation. **TRUE**
   (c) Changing the concentrations of dissolved substances does **not** change the potential observed for an electrochemical cell.

99. **Use the half-reaction method to balance the following reactions in acid solution. You may need to use H⁺ or H₂O to balance the equation**
   (a) 2 MnO₄⁻ (aq) + 5 HSO₃⁻ (aq) + H⁺ → 2 Mn²⁺ (aq) + 5 SO₄²⁻ (aq) + 3 H₂O
   (b) Cr₂O₇⁻² (aq) + 6 Fe²⁺ (aq) + 14 H⁺ → 2 Cr³⁺ (aq) + 6 Fe³⁺ (aq) + 7 H₂O
   (c) Ag(s) + NO₃⁻ (aq) + 2 H⁺ → NO₂(g) + Ag⁺ (aq) + H₂O

100. **Use the half-reaction method to balance the following reactions in basic solution. You may need to use OH⁻ or OH⁻ and H₂O to balance the equation**
    (a) 6 Fe(OH)₂(s) + 2 Cr₂O₇⁻² (aq) → 3 Fe₂O₃(s) + 2 Cr(OH)₆⁻³ (aq) + H₂O + 2 OH⁻
    (b) PbO₂(s) + Cl⁻ (aq) + H₂O + OH⁻ → ClO⁻ (aq) + Pb(OH)₄⁻ (aq)
    (c) 2 Al(s) + 2 OH⁻ (aq) + 6 H₂O → 2 Al(OH)₆⁻³ (aq) + 3 H₂(g)