

Square-1: the basics

Atoms, quanta, periodic table

Moles, formulas, equations

Properties of Gases

States of matter, solutions

Chemical Bonding

Acids and bases

Chemical Change

Electrochemistry

Chem 1

**Concept
Builder**

*Computer-
based lessons
for General
Chemistry*

2001-2002

A guide to the Chem 1 Lessons

The Chem 1 lessons can serve as your principal source of instruction on the topics they cover, but they can do their job best only if they are integrated into the other aspects of your course: reading, lectures, problem-solving, and laboratory activities. The purpose of this Guide is to make this task easier for you (and for your Instructor) by presenting a detailed outline of how each lesson is organized and what each part covers. This will make it easy for you to determine what lessons you need and the order in which you will use them. Because a large portion of the topics listed here are covered in most courses in General Chemistry, this Guide also serves as a handy check list that will help you keep track of your overall progress in the course.

... to help you learn Chemistry

The Chem1 lessons are designed with one purpose in mind: to help you learn Chemistry! In a way, they are a summary of what *I* have learned about how to make Chemistry interesting and understandable during the years I have been teaching the subject to classes varying in size from 30 to 300. For some time now, the computer has been the principal learning tool and communications medium in my course, and this has significantly extended *what* I am able to teach and *how* I teach it. I am pleased to be able to offer these materials to a much wider audience than before. Whether you are enrolled in a regular classroom-based General Chemistry course or in a Distance Education course, or are working on your own, I am confident that you will find these lessons one of the most effective means of achieving a working understanding of the topics they cover.

How to use the lessons

These lessons are founded on the principle that knowledge is not something that can be poured into your head like a liquid. Instead, we must actually construct it for ourselves, something we do best when confronted with an immediate need to do so, such as having to explain something to a friend, solve a problem, or simply to satisfy our curiosity. Thus these lessons consist mainly of a dialogue between me (the Author acting as your teacher), and you, the student. My part of the conversation consists in posing a question or asking you to make a decision, and then guiding you to finding the right answer. The idea is that *you must take an active part in the process*; if I simply “tell” you the answer, you will likely not be able to handle a similar question tomorrow and I will have taught you nothing.

Most lessons follow a sequence in which I provide some information, and I then present you with a question that forces you to make use of that information in some way. It will often happen that the answer will not be immediately apparent to you. Sometimes I even ask a question *before* providing the information required to answer it! Don’t let this bother you; in many years of teaching “live” students, I have found these to be effective devices for getting people to add on to what they already know. This last point is important; what we call “learning” seems to consist in organizing and extending some kind of a “knowledge structure” that we build up in our minds. This is why simply memorizing isolated facts or equations, as you may have done in des-

peration the night before an exam, tends to be of very limited benefit.

You will probably find the lessons most useful if you follow an organized routine. Begin by looking at this Guide to see exactly what a given lesson covers. Then go through one or two lessons and see how well you do. The lessons display in informal “score” that is intended to give you a general idea of your performance. Don’t be discouraged if your score is low the first time around; nobody need ever know! Wait a while, perhaps an hour or a day, and try again. This time, write down your score in the margin of the Guide, and also make a note of what kinds of things you are having difficulty with. You may find it advisable at this stage to do a bit of reading, either in the Digital Textbook that accompanies these lessons, or in whatever real textbook you are using. By repeating this cycle several times (and over a span of several days so you are not simply memorizing the correct answers), you should arrive at a point where your scores are around 80% or better, which is considered “mastery” level. (In the course I teach, 82.5% on the final exam is an “A”!) If, along the way, you find yourself with a question (or answer) that you simply don’t understand, jot it down and ask your instructor. Most teachers appreciate being asked questions that the student has already put some thought into.

How not to use the lessons

These lessons will only be effective, however, if you are willing to put in the effort they demand; simply “going through” them by blindly guessing at answers or pressing the “help” button until the answer is given will be of little use.

Some students are so conditioned to taking extensive notes in lecture that they feel compelled to write down everything they see on the computer screen. *Don’t do it!* I guarantee that it will be a waste of time. This is not to say you shouldn’t take any notes at all; just do so very sparingly, and only for the purpose of reminding yourself of something that needs your further attention.

Finally, don’t come to these lessons “cold”. You will find them far more useful if you have done some reading, and perhaps attempted a few problems beforehand. This will provide you with the beginnings of that knowledge structure that the lessons are designed to build upon.

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How the lessons are organized

When you enter the Chem1 lessons through the main menu, you see a list of the first-level topics shown in the left-aligned column below. Clicking on one of these leads, in most cases, to a sub-menu that allows you to select a specific lesson. For a few topics, there will be more than one level of sub-menu. This hierarchical menu system allows you to quickly locate the particular lesson you want out of the more than a hundred that are available.

The following list shows the present content of Chem1 Concept Builder. Menu titles are printed in bold type; those that lead directly into lessons have the number of lessons within that title shown in parentheses. Menu selections that are themselves single lessons are printed in lighter type.

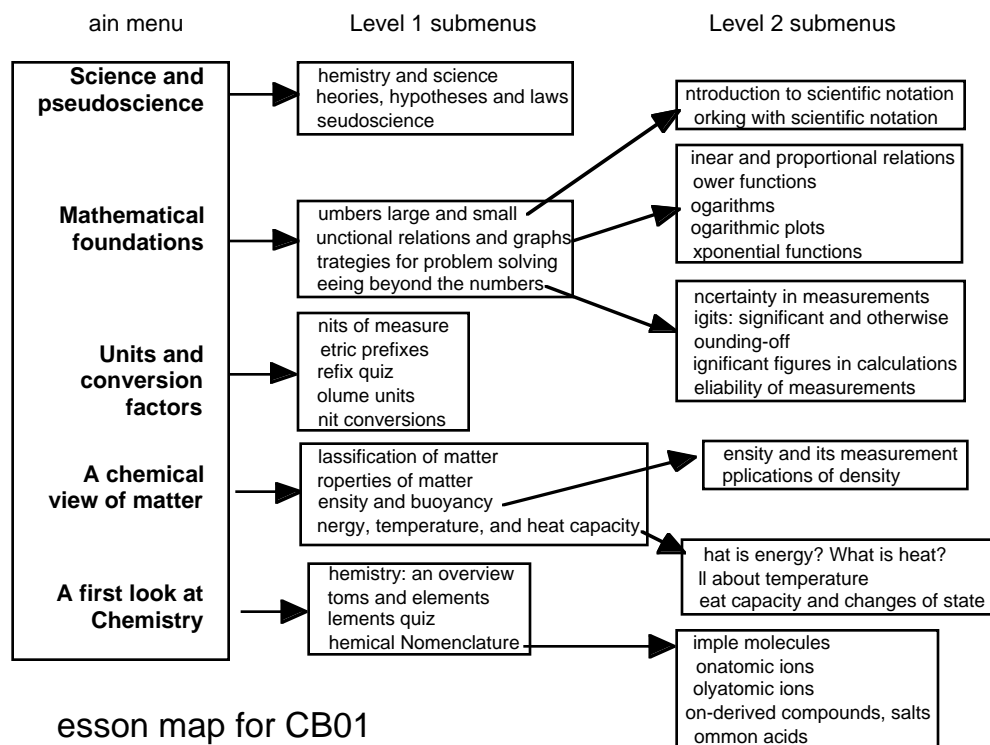
How to use the Chem1 lessons	
Square-1: the basics	1-1
Science and pseudoscience (3)	
Mathematical foundations	
Numbers large and small (scientific notation) (2)	
Functional relations and graphs (5)	
Strategies for problem solving	
Seeing beyond the numbers (significant figures, error in measurements) (5)	
Units and conversions (5)	
A chemical view of matter	
Classification of matter, properties of matter	
Density (2)	
Energy, heat and temperature (3)	
A first look at chemistry	
The basics (2)	
Chemical nomenclature (5)	
Atoms, quanta, periodic table	2-1
The nuclear atom	
The atom ((6)	
Isotopes (4)	
The quantum atom	
Waves and their properties (3)	
The strange world of the quantum (7)	
The simplest atom (3)	
Electron configurations of the elements (3)	
The chemical atom (the periodic table and periodic trends) (5)	
Moles, formulas, equations	3-1
Introduction to the mole concept (3)	
Formulas (3)	
Empirical formulas from experiment (4)	
Chemical equations (2)	
Mass relations in chemical reactions (4)	
Limiting reactant calculations (3)	
Volume relations in gas-phase reactions (3)	
Molar solution stoichiometry (2)	
Properties of Gases (11)	4-1

States of matter, solutions	5-1
States of matter	
Organization of molecular units (3)	
Forces between molecular units (5)	
Basic structural units of solids (2)	
Changes of state: phase maps (4)	
Liquids and solutions	
Liquids and their vapors (5)	
Solution concentrations (4)	
Physical properties of solutions	
Vapor pressure and boiling point (3)	
Freezing point (2)	
Osmotic pressure (3)	
Mixtures of volatile liquids (3)	
Solutions of gases in liquids (2)	
Surface properties of liquids	
Chemical Bonding	6-1
Fundamentals of bonding (7)	
Shapes of molecules (4)	
Hybrid atomic orbitals (4)	
Molecular orbitals (5)	
Acids and bases	
Fundamental concepts of acid-base chemistry	7-1
Introduction	
Proton ping-pong (2)	
Fall of the proton (2)	
Recognizing common acids and bases (5)	
Reactions of acids and bases	
The pH scale (4)	
Acid-base titration (4)	
Acid-base equilibria and calculations	8-1
Introduction to acid-base equilibria (2)	
How the pH controls the composition (4)	
Monoprotic weak acid calculations (4)	
Buffer solutions (4)	
Bases, salts, hydrolysis (6)	
Graphical methods of calculation (4)	
Polyprotic systems (4)	
Carbonates and natural waters (5)	
Chemical Change	
Chemical Energetics (13)	10-1
Chemical equilibrium (5)	9-1
Electrochemistry	11-1
Basic principles (7)	
The Nernst Equation and its applications (5)	

Square-1: getting started

It all begins here; this group of lessons develops the fundamental concepts you will need to get started in Chemistry. Many Chemistry courses skip over much of this material, or at best cover it very rapidly during the first week or two, assuming either that you have seen it all before or that it is so simple that you can get it out of the textbook. This is fine for those who have studied some Chemistry in the past, but many students have not, or have been away from it for a while. All too often, by the time you realize this, the course has moved on to new material and you never do master these fundamental topics, leaving yourself crippled for the rest of the semester.

These lessons are designed with these problems in mind. Although they are elementary, they treat their various topics at an adult level of sophistication, and they are organized in such a way that you can return to them at any time and review the particular parts you need. If at all possible, you will be wise to go through *all* of the lessons in this set, even those whose topics do not appear in your course syllabus. This is really basic stuff that will find application in all kinds of unexpected contexts, not only in the course you are currently taking, but also in future courses and in many aspects of daily life.



Lesson map for CB01
Square-1 lesson set

Note: in the following pages, the parenthesized number at the end of a lesson title indicates the number of “questions” contained in that lesson.

Part 1 - Science and pseudoscience

Lesson 1 What is science? (0) Early knowledge, alchemy; the Enlightenment and science; cognitive and noncognitive belief systems, pseudoscience.

Lesson 2 Hypotheses, theories, and laws Origins of science; Bacon, Copernicus, Galileo; the role of experiment. The natural sciences; Chemistry and Physics. Distinguishing between hypotheses, theories, and laws.

Lesson 3 Pseudoscience Distinguishing pseudoscience and science; astronomy and astrology compared.

Part 2 - Mathematical foundations

2-A. Numbers large and small

Lesson 4 Introduction to scientific notation (8)

Powers of 10 and the numbers they correspond to; multiplication by a factor; numbers smaller than 1; drill.

Lesson 5 Working with scientific notation (11)

Multiplication, division, exponentiation, addition and subtraction. Each operation begins by combining simple powers of 10, and then two or more numbers in scientific notation.

2-B. Functional relations and graphs

Lesson 6 Direct proportionality: equation of a line (17) Detecting linear proportionality from experimental data; the proportionality constant; the equation $y = mx$. Constructing a linear plot, extrapolating to origin; the slope. Problem examples, including mass stoichiometry. Graphs with non-zero intercepts; $y = mx + b$. Estimating absolute zero of temperature by extrapolating V vs. T plot. Drill: determining signs of m and b by visual inspection.

Lesson 7 Power functions (15) Exploring the properties of functions $y = m^x$ with emphasis on their ranges and graphs. The inverse and square root functions; integer and non-integer x . Drill on recognizing functions from their graphs.

Lesson 8 Logarithms (17) Powers of 10 and exponents; logs as exponents; the base-10 system. Logarithms of integral powers of 10, of 10 itself, and of zero. Logs of numbers smaller than zero. Logs of numbers between 1 and 10; use of $\log 2 = 0.3$ for estimating. Finding logs of numbers outside the

range 1-10; combining logs. The characteristic and mantissa. Antilogarithms.

Lesson 9 Logarithmic plots (4) How use of logs is necessary to plot wide range of data values. Comparison of linear and log plots of vapor pressure data; estimating value from the log plot. Constructing logarithmic bar graph from relative values.

Lesson 10 Exponential functions (5) Compound interest and the compound interest law; convergent series; definition of e ; properties of exponential functions $y = e^{ax}$; slope equal to value. Estimating a point on an exponential decay plot; half-life.

Lesson 11 Strategies for problem solving Questions to ask before undertaking a solution. Example problems emphasizing direct and inverse proportion, units analysis, direct proportion with interpolation, combinations.

2-C. Seeing beyond the numbers

Lesson 12 Uncertainty and error in measurements (12) The difference between accuracy and precision; random and systematic error; control of latter by means of blank readings. Importance of replicate measurements. Absolute and relative uncertainty.

Lesson 13 Digits: significant and otherwise (10)

Why no measurement of a continuous value can be exact. Estimating a length with scales of differing fineness; number of digits known exactly; significant digits. Expressing precision in "parts per" form. Reading a volume; effect of volume unit on number of significant digits.

Lesson 14 Rounding-off (7) Rules for rounding off, presented through example problems. Dual role of zeros as significant digits and as placeholders; use of scientific notation to avoid ambiguity.

Lesson 15 Significant figures in calculated results (17) The relative uncertainty expressed in a measured value; results of calculations on this value should be expressed to comparable uncertainty; rounding-off as a means of ensuring this. Rules of multiplication-division, addition-subtraction; "infinite-precision" integers. Need to occasionally bend the rules; "partly"-significant digits; implied uncertainties expressed as absolute and relative quantities. Special considerations when the range of uncertainty spans a power of ten. Examples: area of a rectangle, density of an object. Retaining non-significant digits in continued calculations.

Lesson 16 Reliability of measurements (22)

Reading a frequency graph; the mean value of pairs of measurements, dispersion of the means. Effects of sample size. The standard error curve and its use; deviations from the mean; the standard deviation and its meaning; confidence intervals.

Part 3 - Units and unit conversions

Lesson 17 Units of measure (8) Metric and SI base units of mass and length; mass *vs.* weight; units related to temperature: degree and kelvin; SI unit of time.

Lesson 18 Using the metric prefixes (9) Prefixes (mega-, milli-, etc.) and the factors by which they multiply units.

Lesson 19 Metric prefix drill (10) Randomly asks for name or power of ten.

Lesson 20 Volume units (8) Volume as an SI derived unit; the liter, milliliter and cubic centimeter; number of cm^3 in a m^3 .

Lesson 21 Unit conversions (12) Setting up and using unit conversion factors. Conversions involving multiple units (e.g., velocity) and volume.

Part 4 - A chemical view of matter

Lesson 22 Classification of matter (22) Definition of a *phase*; phase boundaries. Homogeneous and heterogeneous matter, distinguishing them by their appearance; pure substances and mixtures, solutions. Classification of various substances according to these criteria. Further subdivision of pure substances into elements and compounds. Distinction between *atom* and *element*. Operational (*vs.* conceptual) definitions of the various kinds of matter.

Lesson 23 Properties of matter (16) Importance of properties as a means of characterizing matter; distinguishing between properties and non-properties. Extensive and intensive properties; quotient of two extensive properties is an intensive property; examples of density and electrical conductivity.

4-A. Density

Lesson 24 Density and its measurement (11)

Interpreting a volume-mass plot; calculating density from volume and mass; equivalence of g cm^{-3} and kg L^{-1} units; calculating volume and mass. Effect of temperature on density. Water: its density and density-temperature plot. Densities of metallic *vs.* non-metallic solids. Measuring the density of an irregular object by displacement of liquid.

Lesson 25 Applications of density (18) Displacement of a fluid; densities of ice and water, calculating volume increase of water on freezing. Problem: What fraction of a floating ice cube will be under water? Specific volume. Apparent loss in weight of an object when immersed in a fluid; buoyancy. Archimedes' measurement of the density of King Hiero's crown. Effect of buoyancy when weighing a large object in air. Some consequences of the 4°C density maximum of water; fall- and spring turnover of water in lakes. Definition of specific gravity; effect of water reference temperature. Estimating the diameter of a neon atom from the density of its liquid.

4-B. Energy, heat and temperature

Lesson 26 What is energy? What is heat? (24)

Kinetic and potential energy and their interconversion; conservation. Energy and work. Thermal energy; impossibility of utilizing it to restore potential energy of source. Heat as a flow of energy due to temperature difference. Chemical energy as electrostatic potential energy; exothermic and endothermic reactions; definition of a fuel.

Lesson 27 Temperature and its measurement

(9) Physical significance of temperature; its measurement through a property (e.g., density) that changes with temperature. Temperature scales defined by magnitude of the *degree* and by the zero point. The Celsius and Fahrenheit scales, converting between them. The absolute temperature scale.

Lesson 28 Heat capacity and changes of state

(11) Energy units and thermal energy; effect of mass on temperature change due to flow of heat into a body; heat capacity as an extensive property; specific heat. Calculating quantity of heat required to bring about a given temperature change. Heat required to vaporize a given mass of ice.

Part 5 - A first look at chemistry

5-A. The basics

Lesson 29 Chemistry: an overview (17) Definition of chemistry; its relation to other disciplines. Macroscopic and microscopic concepts: composition vs. structure, elements and compounds vs. atoms and molecules. Conceptual hierarchy of Chemistry: composition/structure, properties, change. Physical and chemical aspects of properties and change; drill on physical vs. chemical changes. Aspects of change; energetics and equilibrium, dynamics; macroscopic and microscopic views of the latter.

Lesson 30 Atoms and elements (16) The chemical element as the simplest form to which a substance can be reduced; pitfalls of this concept. Approximate number of elements. Organizing the elements; atomic number and atomic (relative) weight, determination of latter through experiment. The periodic table. The atom and its structure; the proton, neutron, and electron. Proton (atomic) number, neutron number, mass number; isotopes. (Note: this is a greatly abbreviated treatment of topics treated in much greater detail in CB02.)

Lesson 31 Elements quiz (14) This quiz presents descriptions of various elements in random sequence; the user identifies the element by clicking on the appropriate symbol in a periodic table.

5-B. Chemical nomenclature

Lesson 32 Simple molecules (13) Systematic names of CO_2 , CO , SiCl_4 , SO_3 , PCl_5 , SF_6 , H_2O . Special names: NH_3 , NO , N_2O , HCN , CH_4 .

Lesson 33 Monatomic ions (13) Definition of an ion; cations and anions. Formulas or names of the ions of O, Al, S, Sn, Fe, Cu, Hg.

Lesson 34 Polyatomic ions (12) Names of H_3O^+ , NH_4^+ , CO_3^{2-} , HCO_3^- , NO_3^- , SO_4^{2-} , OH^- , CN^- , ClO^- and ClO_4^- in context of chlorite and chlorate, MnO_4^- , $\text{Cr}_2\text{O}_7^{2-}$.

Lesson 35 Salts and ionic-derived solids (13) Electroneutrality and its role in determining formulas. Formulas of calcium fluoride, ferrous sulfide, sodium oxide, ferric sulfide, mercurous chloride, ammonium sulfate, silver cyanide, potassium dichromate, sodium carbonate, sodium bicarbonate, trisodium phosphate, potassium dihydrogen phosphate.

Lesson 36 The common acids (7) Names of HNO_3 , HNO_2 , H_2SO_4 , H_2CO_3 , HCl , CH_3COOH , H_3PO_4 .

Atoms, quanta, and the periodic table

These lessons contain everything you need to know (but are perhaps afraid to ask!) about the modern (quantum) theory of the atom. Different courses will present these topics in different orders, or even in different parts of the same course, so it is important for you to obtain guidance from your instructor.

Part 1 - The Nuclear Atom

1-A. The atom

Lesson 1 Atoms: the history of an idea (0).

Lesson 2 What atoms are made of (8) Protons, neutrons and electrons; volume occupied by electrons determines volume of the atom. Definitions of: nucleus, nucleon, nuclide, isotope.

Lesson 3 At the center of things: the nucleus (14) Constitution of hydrogen and helium nuclei. Rutherford's experiment and its interpretation.

Lesson 4 Problem: density of a neutron star (3)

Lesson 5 Characterizing the atom Mass number and the atomic mass unit; atomic number. Nuclide notation.

Lesson 6 Understanding nuclide notation (6) Definitions of mass number, atomic number, atomic mass unit. Nuclide notation.

1-B. Isotopes

Lesson 7 Tutorial on isotopes (4) Non-integral atomic weights and isotopes; deuterium; role of C^{12} ; mass spectrometer.

Isotope Problems

Lesson 8 Abundance of HDO and D₂O in water (3) The isotopic abundance of 2H (deuterium) in natural hydrogen is 0.01 percent. How many HDO molecules will be in 1 million molecules of water, and how many D₂O molecules are in 1 mole of water?

Lesson 9 Average atomic weight of boron (1) Calculate the average atomic weight of boron from the isotopic abundance data given.

Lesson 10 Isotopic abundance from chlorine mass spectrum (12) The mass spectrum of Cl_2 shows peaks at masses 70, 72, and 74, with heights in the ratio of 9 to 6 to 1. Deduce the isotopic composition of natural chlorine.

Part 2 - The Quantum Atom

2-A. Waves and their properties

Lesson 11 Waves and their properties (15)

Standing waves and boundary conditions on a vibrating guitar string; characterizing a wave: nodes and antinodes, amplitude, wavelength; Frequency and its relation to wavelength. Fundamental and harmonics.

Lesson 12 Summary (0)

Lesson 13 Problems (2) *Problem 1:* Radio waves propagate through space at the speed of light, $3.00E8 \text{ m s}^{-1}$. Find the wavelength of radio waves whose frequency is 30 Mhz.

Problem 2: Calculate the frequency of a sound wave whose wavelength in air is 10 cm.

2-B. The strange world of the quantum

Lesson 14 The electromagnetic spectrum and the nature of light (2)

Lesson 15 Black body radiation and the origin of quanta (6) Line- and continuous spectra. Planck and the black-body problem. Relation between temperature and frequency; distribution curves, continuous vs line spectra.

Lesson 16 Light as a quantum particle: the photoelectric effect (10) Thompson's discovery of the electron; the photoelectric effect; Einstein's relation $e = hv$.

Problem 1 The maximum wavelength of light able to eject electrons from a sodium metal surface is about 600 nm. What is the binding

energy of the electrons in Na?

Problem 2 The dissociation energy of the chemical bond in hydrogen iodide, HI, is 299 kJ mol⁻¹. Calculate the longest wavelength of light that should be able to induce photodissociation in HI.

Lesson 17 Wavelengths of particles (2) The de Broglie relation.

Problem: Calculate the wavelength of an electron moving at a velocity of 300 m s⁻¹

Lesson 18 Relativity and mass-energy equivalence (5) **Problem:** Estimate the change in total mass for a chemical reaction with $\Delta H = -1000$ J.

Lesson 19 Indeterminacy (“Uncertainty”) principle (7) **Problem1:** An electron is moving at a velocity of 300 ± 0.03 m s⁻¹. With what precision can we specify the location of the electron at any instant?

Problem 2: Calculate the velocity and maximum kinetic energy of an electron that is confined to a one-dimensional box of length 100 pm.

Lesson 20 The tunnel effect (2) Potential wells and their penetration by quantum particles; applications to bonding, nuclear decay.

2-C. The simplest atom

Lesson 21 The hydrogen atom: a first look (8)

Observable properties: volume occupied by electron, sign of ionization energy, line spectrum. How the potential energy depends on distance of electron from nucleus; meaning of zero potential energy. Why the electron doesn't fall into the nucleus. Line spectra and their relation to orbital energies. Ionization limit and continuum.

Lesson 22 Atoms and music: the simplest orbitals (5) (*s* orbitals.) Nature of an orbital; nodes and antinodes in 2-d representations; plots of probability density and total probability, average radius. Ground state and excited states of hydrogen.

Lesson 23 Quantum numbers and orbital types (4) Physical meanings and allowed values of the various quantum numbers. Shapes of *s* and *p* orbitals.

2-D. Electron configurations of the elements

Lesson 24 Rules for orbital filling (2) The spin quantum number and the Exclusion Principle.

Lesson 25 The first eighteen elements (17) A systematic exploration of the orbital configurations.

Lesson 26 The rest of the elements: *d*- and *f* orbitals (26) Emphasis on locating elements at which *d* and *f* orbitals begin to fill.

Part 3 - The Chemical Atom

3-A. Atoms and the periodic table

Lesson 27 Introduction (8) The periodic law, shell model of the atom; noble gas configurations of anions and cations.

Lesson 28 Ionization energy (12) Definition and sign, periodic trends.

Lesson 29 Electron affinity (3) Meaning, sign and periodic trends.

Lesson 30 Atomic radius (7) Various ways of defining atomic and ionic radii. Periodic trends; relative sizes of atoms and ions; isoelectronic series.

Lesson 31 Electronegativity (5) Definition. Bond polarity and the Pauling scale. Fluorine and oxygen.

Solutions to problems

Lesson 16 - Photoelectric effect:

$$\text{frequency} = (3E8 \text{ ms}^{-1}) / (6E8 \text{ m s}^{-1}) = 5.0E14 \text{ s}^{-1}$$

$$\text{energy per photon: } (6.626E-34 \text{ J s}) \times (5.0E14 \text{ s}^{-1}) = 3.31E-19 \text{ J}$$

$$\text{energy per mole of photons: } (3.31E-19 \text{ J}) \times (6.02E23) \times (1 \text{ kJ}/1000 \text{ J}) = 199.4 \text{ kJ}$$

Lesson 17 - energy to dissociate one molecule:
(299000 J) / (6.02E23) = 4.97E-19 J

$$\text{frequency: } (4.97E-19 \text{ J}) / (6.63E-34 \text{ J s}) = 7.50E14 \text{ s}^{-1}$$
$$\text{wavelength in nanometers: } (109 \text{ nm}/1 \text{ m}) / (3.00E8 \text{ m s}^{-1}) / (7.5E14 \text{ s}^{-1}) = 400 \text{ nm}$$

Lesson 18 -

$$m = (1E6 \text{ kg m}^{-1} \text{ s}^{-1}) / (9E16 \text{ m}^{-1} \text{ s}^{-1}) = 1.11E-10 \text{ kg}$$

Lesson 19 -

Problem 1: Percent uncertainty in the velocity:
.03/300 x 100% = 0.01 %; momentum of electron: $p = mv = (9.11E-31 \text{ kg}) / (300 \text{ m s}^{-1}) = 2.73E-28 \text{ kg m s}^{-1}$
 $\delta x = h/\delta p = (6.63E-24 \text{ kg m}^2 \text{ s}^{-1}) \times (2.7E-32 \text{ kg m s}^{-1}) = 0.024 \text{ m}$

Problem 2: $\delta p = h/\delta x = (6.6E-34 \text{ J s}) / (1E-10 \text{ m}) = 6.6E-24 \text{ J s m} = 6.6E-24 \text{ kg m s}^{-1}$
absolute value of the momentum is between 0 and 3.3E-23 kg m s⁻¹.

$$\text{max velocity: } v = p/m = (3.3E-22 \text{ kg m s}^{-1}) \geq (9.1E-31 \text{ kg}) = 3.6E6 \text{ m s}^{-1}$$
$$\text{max kinetic energy: } KE = mv^2/2 = pv/2 = (3.3E-24 \text{ kg m s}^{-1}) \times (3.6E6 \text{ m s}^{-1}) / 2 = 5.9E-18 \text{ J}$$

Moles, formulas and equations

Chemical arithmetic and stoichiometry: for many, the “worst” part of Chemistry! Still, you *must* know this stuff, and know it well; it’s impossible to do any practical Chemistry without it. This lesson set represents our best effort to present the subject in as interesting a way as possible, without reducing it to kindergarten-style games or, even worse, to an algorithmic or formula approach. In order to avoid the latter pitfall, considerable stress is placed on skills that seem often to be overlooked in textbooks and for which there is rarely time in the classroom.

This lesson set will be especially useful in college-level courses that assume their entering students have previous experience in stoichiometric calculations. As any teacher of such a course knows, prerequisites of this kind mean little, especially when some time has elapsed since the previous course. These lessons provide an excellent means of shaking off the rust and bringing the class up to a reasonable level of competence without devoting much class time to the subject.

Part 1 - Introduction to the mole concept

Lesson 1 The mole: what is it? (12)

Relative masses of atoms; relative weight of Li from its combining weight with H. Mass of a mole numerically the same as relative mass; examples O, O₂. Definition of mole in terms of C¹². Avogadro’s number and its units. Number of moles in *N* items, number of molecules in *N* moles.

Lesson 2 Visualizing the mole (8) Time required to count 1 mole, length of beach containing 1 mole of sand grains (these are also good exercises in unit conversions!)

Lesson 3 Calculations with arbitrary random numbers and elements. (7) Number of atoms in *N* mol, number of moles in *N* atoms, number of atoms in smallest weighable mass of an element,. Mass of one atom of an element.

Part 2 - Formulas

Lesson 4 How to write them and read them (8) Dinitrogen tetroxide, ammonium sulfate. Ethanol and dimethyl ether; isomers. Simplest formulas and complex structures; LiCl, CuCl₂, H₂B₄O₇.

Lesson 5 Molar mass (2) What it means, how it is calculated.

Lesson 6 Calculations based on formulas (15) Find lightest element in Group 2 that makes up at least half of weight of the oxide; mass fraction and

mass percent of the metal in this compound. Examples based on SbF₃: Mass of an element in a given mass of a compound, mass fraction of element in compound. Given mass fraction, find mass of element in arbitrary mass of compound expressed in units other than grams. Problem: how many tons of Ca₃(PO₄)₂ must be processed to manufacture fertilizer containing 100 T of phosphorus? (Carried out in steps, beginning with calculation of molar mass.)

Part 3 - Empirical formulas from experiment

Lesson 7 True formulas vs. empirical formulas (8) Meaning of simplest formula; examples of N₂O₄, C₆H₁₄. Mole ratios in simplest formulas; finding the simplest formula corresponding to a given mole ratio; example, C:H= 0.6 is C₆H₁₀. Simplest formulas from weight information; examples of C-H compound with mass content of C and H given; moles of one element in arbitrary mass of compound.

Lesson 8 Formulas and mole ratios (13) Recognizing decimal numbers that express integer ratios; practice in obtaining mole ratios A:B and B:A from formula A_{*m*}B_{*n*}.

Lesson 9 Formulas from mass composition (11) **Problem 1:** A crystalline hydrate of CoCl₂ was found to lose weight on heating (data given). Find the value of *n* in the formula CoCl₂·*n*H₂O. **Problem 2.** Find empirical formula of a hydrocarbon from moles of C and H.. (13)

Problem 3. Find empirical formula of a compound containing only C, H, and O from the element masses.

Lesson 10 Empirical Formulas from percent composition. (3) Problem examples: Iron-oxygen compound (Fe_2O_3 or Fe_3O_4), and $\text{Ag}_4\text{V}_2\text{O}_7$.

Part 4 - Chemical Equations

Lesson 11 How to write and balance them

(17) Terms: reactants, products, coefficients, conservation of mass. Pictorial balancing of $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}$, $\text{N}_2 + \text{H}_2 \rightarrow \text{NH}_3$. Balancing procedure for more complicated cases: $\text{NH}_3 + \text{O}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O}$.

Lesson 12 Net ionic equations (16) Definition of "chemical change" in dissolution - precipitation. Ions; balancing ionic charges. Definition of *net* chemical change. Dissolutions of two salts with and without precipitate formation; completeness of such reactions. Elimination of "spectator" ions.

Part 5 - Mass relations in chemical reactions

Lesson 13 Introduction: a simple synthesis ($\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$) (6) Interpreting equations in terms of moles and mass. Illustration of mass conservation, reacting masses of components, their expressions in various mass units.

Lesson 14 Oxidation of waste ($\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) (4) Relative masses of reactants; **Problem:** calculate kg of O_2 consumed per kg dry weight of carbohydrate waste.

Lesson 15 Production of H_2SO_4 (2) **Problem:** Quantity of S required to manufacture 100 T of sulfuric acid (2)

Lesson 16 Steam reforming of natural gas
Problem: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$

Part 6 - Limiting reactant calculations

Lesson 17 Introduction(3) Meaning and significance of a limiting reactant; identifying the limiting reactant. Example reactions:
 $\text{CaF}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow 2\text{HF}(\text{g}) + \text{CaSO}_4(\text{g})$,
 $\text{fuel} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$.

Lesson 18 Mole-mole example (3)
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

Lesson 19 Mass-mass example (5)
 $\text{CaF}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow 2\text{HF}(\text{g}) + \text{CaSO}_4(\text{g})$

Part 7 - Volume relations in gas-phase reactions

Lesson 20 Law of Combining Volumes (7)

Find combining volume integer ratio when n ml of A reacts with m ml of B. Avogadro's law; if n g of ethane occupies a volume of v ml, calculate the volume of an equal mass of CO_2 when measured under the same conditions. Use of combining volumes to determine formulas of H_2 , O_2 , H_2O , Cl_2 , HCl .

Lesson 21 Adjusting your carburetor (6)
A volume-volume problem

Lesson 22 Determining volume of air required for each ml of fuel consumed. (7)
(Problem in several steps)

Part 8 - Molar solution stoichiometry

Lesson 23 Solution molarity (9) Solvent and solute, definition of molarity. Calculation of molarity, number of moles contained in a given volume, volume of n moles.

Lesson 24 A titration problem (2) Chloride in water by Ag^+ titration.

Properties of Gases

Most of this unit is devoted to the *ideal gas*, a fictional substance which is nevertheless the only state of matter about which we know everything there is to know, and which serves as the starting point for the treatment of all other matter in its various states. Lessons 1 through 9 will be applicable to almost any introductory course, while the last two lessons may be skipped in some more elementary courses.

Lesson 1 Introduction (11) Pressure as the fundamental observable property of a gas; definition and kinetic-molecular origin of gas pressure. How pressure is measured. Effect of temperature on P and V

Lesson 2 Effect of temperature on P and V (8)
Charles' law in graphical and algebraic forms, and expressed as $1/273$ change in volume per degree; extrapolation to absolute zero.)

Lesson 3 Mole-volume relations in gas-phase reactions (9) Avogadro's law; comparing the volumes of equal masses of different gases. Gas-volume stoichiometry.

Lesson 4 Pressure-volume relations (6) Exploring the relation between pressure and volume; Boyle's experiment and Boyle's Law.

Lesson 5 The ideal gas law (23) the PV -product and its dependence on the temperature; combining Boyle's, Charles' and Avogadro's laws. The gas constant and its units. Exploring the PVT -surface (see figure at right.)

Lesson 6 Diffusion (7) Kinetic energy, mass, and molecular velocities; Graham's Law. Relative diffusion rates of NH_3 and HCl .

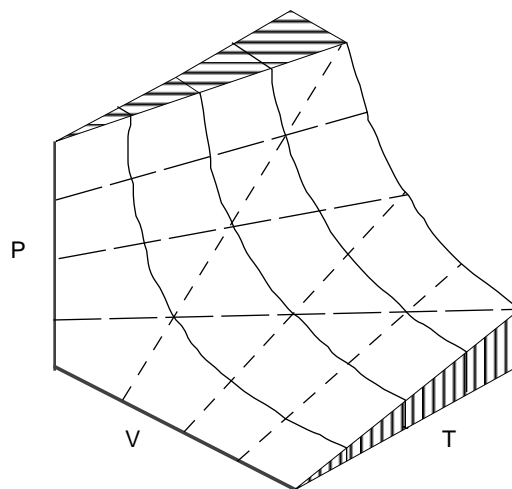
Lesson 7 Mixtures of gases (7) Partial pressure; Dalton's Law. Application to scuba diving.

Lesson 8 Gas density (7) Molar volume and molar mass. Effects of P and T on the density.

Lesson 9 Atmospheric pressure and the barometer (7) The relation between pressure and altitude. Operation of mercury and water barometers.

Lesson 10 Molecules in motion (13) How velocities are averaged. The kinetic energy of a gas and the effect of collisions in redistributing molecular velocities. Understanding velocity distribution curves. Boltzmann distribution and the temperature. Average molar kinetic energy.

Lesson 11 Real gases and intermolecular interactions (21) Assumptions of the kinetic-molecular theory not applicable to real gases. Excluded volume and intermolecular attractions; the conditions under which they become significant. Understanding PV vs P plots; effects of temperature and molar mass. The van der Waals equation.



This PVT -surface is discussed in Lesson 5. It is a graphical representation of the ideal gas equation $PV = nRT$ for $n=1$. Because three variables are involved, the graph must be three-dimensional. You should be able to visualize the 2-dimensional slices corresponding to the laws of Boyle and Charles.

Solids, liquids and solutions

Most of us first approached Chemistry through our encounters with the world of solids and liquids that we could see and feel. Only later, our curiosity piqued, do we delve into the wonders of quanta, structure, and reaction theory which now form the core of modern chemical science. Nevertheless, the study of bulk matter remains an essential part of preparation for fields as diverse as physiology and engineering.

The lessons in this set attempt to cover the realm of Chemistry that bridges the microscopic and macroscopic. There is a lot more here than will fit into most General Chemistry courses, so you should seek guidance from your instructor as to which lessons to do, and in what order.

Part 1 - States of matter

1-A. Organization of molecular units

Lesson 1 Introduction: solids, liquids and gases (8). Effects of P and T on state; discontinuities in properties as indication of change in state; enthalpies of fusion, vaporization and sublimation and the relations between them.

Lesson 2 Liquids and their properties (9)

Temperature range of liquids and intermolecular forces; long- and short-range order; “structure” of a liquid and effects of temperature; relative kinetic and potential energies in liquid and gaseous states. Viscosity of liquids, temperature dependence of viscosity in liquids and gases.

Lesson 3 Distinguishing properties of solids, liquids and gases (9) In this lesson, the terms density, cohesiveness, surface tension, degree of disorder, viscosity, and kinetic energy per molecule are briefly explained, and the student is asked to rate each of the three states of matter in terms of the approximate degree to which it possesses the property in question.

1-B. Forces between molecular units

Lesson 4 Origin of intermolecular forces (15)

Condensed states of matter as evidence of intermolecular attractions; meaning of their low compressibilities. Repulsive and attractive forces and their relative strengths as indicated by Mie’s equation coefficients. Comparison of potential energy curves for “intermolecular attractions” and chemical bonding. Electrostatics as the active force; van der Waals forces. Classification of particles as being a nonpolar molecule, an ionic substance, or a polar molecule.

Lesson 5 The universal attractive force:

why does argon condense? (4) Time-average vs. instantaneous electron distributions; the dispersion force and its dependence on distance and number of electrons; bp and heat of vaporizations of the noble

gas elements. Bp’s of hydrocarbons and fluorocarbons compared; polarizability.

Lesson 6 Permanent dipole moments (11)

Electron distributions in H₂ and in HF; polar molecules. Meaning of $\delta\pm$ notation. Dipole moment $\mu = qr$ and its magnitude expressed in C-m and Debye units. How dipole moments are measured. Charge displacement and percent ionic character of HF. Polarity of water and of the halomethanes.

Lesson 7 Forces involving dipoles (6) Relative strengths of attractions involving ions and dipoles. Ion-dipole forces in NaF and NaOH; ion hydration, hydrogen bonding, dipole-induced dipole attraction

Lesson 8 Hydrogen bonding and water (9) A special case of dipole-dipole interaction; F, O, and N as main elements promoting H-bonding. Effect on boiling points, comparison of XH compounds. How temperature affects the density of water. Hydrogen bonded solids: oxalic acid, DNA

1-C. Basic structural units of solids

Lesson 9 Introduction (11) Crystalline and amorphous solids; polymers and glasses. Molecular crystals; solid forms of the elements; metallic solids, ionic solids. Extended structures: chains and layers; covalent solids.

Lesson 10 Practice quiz (8) The user is asked to classify various substances (drawn from a randomly-selected list) according to the following scheme: cohesiveness, coefficient of thermal expansion, surface tension, viscosity, average kinetic energy per molecule, degree of disorganization. The substances presented are: noble gas solid, aluminum, CuCl₂, poly(ethylene), CCl₄, SiC, NaCl, glass.

1-D. Changes of state: phase maps

Lesson 11 Introduction to phase maps (5)

Relating vapor pressure-vs.-temperature plots to boiling point curve in P-T space. The critical point and supercritical fluids. Addition of melting point line to obtain a complete phase diagram; locating the normal melting point.

Lesson 12 The phase map of water (5) The triple point; locating the boiling, melting and sublimation lines. Significance of slope of the melting point curve.

Lesson 13 Some other phase maps (7) Carbon dioxide: identifying 1-atm line; why Dry Ice is “dry” CO₂ fire extinguishers can seem empty on warm days. Estimating temperature of the solid and effect of pressure on the melting point. Supercritical CO₂. Diamond: stability of graphite, number of triple points.

Lesson 14 A trip across the phase map:

warming-cooling curves (6) What happens as we move along the temperature coordinate at constant pressure. Constructing a warming plot; relative lengths of the melting and boiling halts

Part 2 - Liquids and solutions

2-A. Liquids and their vapors

Lesson 15 Vapor pressure: escaping tendency of molecules from the liquid (10) How molecules enter the vapor space; vapor pressure and its measurement using a J-tube manometer. and a barometer. Vapor pressure as an intensive equilibrium property; dependence on temperature. Relation between vapor pressure and boiling point; the normal boiling point; volatility.

Lesson 16 Water in the atmosphere: understanding relative humidity (6) Humidity (partial pressure of H₂O); relative humidity (ratio of partial pressure to vapor pressure); finding the relative humidity at a given temperature. Problem: determine relative humidity of inside air brought into room from outside at lower temperature.

Lesson 17 Changes of state: boiling and condensation (9) Distinction between evaporation and boiling; the normal boiling point; finding the pressure at which water boils at room temperature. Vapor pressure inside a bubble; why liquids boil above their boiling points; bumping. Condensation temperature at a given relative humidity; the dew point; supercooling and nucleation.

2-B. Solutions: types and formation

Lesson 18 Why solutions form— sometimes!

(9) Mostly qualitative discussion of energetics of dissolution relating to dispersion of solute and its incorporation into solvent; role of hydration energy in dissolution of ionic solids and net dissolution enthalpy. Water solubilities of alcohols vs. hydrocarbons; effects of chain length. Nature of positional disorder; gas, liquid and solid phases as solute/solvent. Competition between changes in energy and disorder in practical situations.

Lesson 19 Drill exercise on energetics of solution formation (24)

For various combinations of solute/solvent as gas, polar/nonpolar liquid, or ionic/molecular solid, the student is asked to provide a qualitative assessment of the energy to disperse the solute, the energy associated with introducing the solvent into the solute, and the change in disorder. A full explanation is provided for each kind of solute/solvent system.

2-C. Solutions: concentrations

Lesson 20 Introduction: what do we mean by concentration? (7)

Solutions as homogeneous mixtures; identification of solute and solvent as minority and majority components. General meaning of concentration; concentrated and dilute solutions, solubility, miscibility.

Lesson 21 How concentrations are expressed

21-1 Percent concentration (5)

21-2 “Parts-per” concentration (5)

21-3 Mole fraction (4)

21-4 Molal concentration (3)

21-5 Molar concentration (4)

Lesson 22 Molar concentration calculations

(16) This exercise consists of a sequence of simple problems; in most cases, the parameters are generated randomly; the values given below are typical.

- grams of SrCl₂ to make 1 L of 0.097 M solution;
- grams of SrCl₂ to make 2.50 L of 0.115 M solution;
- calculate the molarity of 3.0 L of a solution containing 2.30 mol of KNO₃;
- calculate the molarity of 62 mL of a solution containing 0.098 mol of Na₂CO₃;
- In an analysis, 16.60 mL of 0.347 M NaOH solution is required to neutralize the acid in a sample of vinegar. How many millimoles of OH⁻ were used?
- Find the molarity after the volume of 175 mL of a 0.80 M solution is doubled.

- Calculate the molarity after sufficient water has been added to 145 mL of a 0.70 M solution to bring its total volume to 500 mL.
- To what volume must we dilute 40.0 mL of a 0.65 M solution of HCl in order to reduce the concentration to 0.290 M?
- What volume of 12 M sulfuric acid must be added to water in order to make 300 mL of a 1.00 M solution of H₂SO₄?

Lesson 23 Common types of concentration problems

23-1 Mass Fraction (3): Find the mass-percent of solute when 8.4 g of CuSO₄·5H₂O is dissolved in 52.0 mL of water.

23-2 Specified mass of solute (3): How many mL of 70.6% perchloric acid is required to prepare a solution that contains 2.2 g of HClO₄?

23-3 Mass-% to mole measure (7): Calculate the molarity, molality, and mole fraction of fructose in a solution that contains 39 percent by weight of C₆H₁₂O₆ and whose density is 1.2 g mL⁻¹.

23-4 Dilution of a stock solution (3): Commercial concentrated hydrobromic acid has a density of 1.50 g mL⁻¹ and contains 47 percent HBr, molecular weight 80.91. How many mL of this acid is required to prepare 1.00 L of 1.45 M HBr?

23-5 Molal solution (4): A 2.10 molal solution of sodium hydroxide (molar mass 40 g) has a density of 1.07 g mL⁻¹. Calculate the molarity and weight-percent of NaOH in this solution.

2-D. Solutions: physical properties

Lessons 24 through 31 deal with the **colligative properties** of solutions of non-volatile solutes.

Vapor pressure and boiling point

Lesson 24 Why solutes affect the vapor pressure of the solvent (6) Vapor pressure as a measure of escaping tendency from a phase. Origin of vapor pressure; vapor phase more disordered, increase in disorder greatest for volatilization of pure solvent, so its dilution by a nonvolatile solute reduces the vapor pressure. Colligative properties and nonvolatile solutes.

Lesson 25 How to predict the vapor pressure of the solution (5) Construction of a vapor pressure-vs.-mole fraction plot; Raoult's law. Problems: calculate the vapor pressure of a mixture of ethylene glycol and water at 16°C in which 18 percent of

the molecules are H₂O, and in which the mole fraction of glycol is 0.89. Ideal solutions; relative attractions of like and unlike molecules leading to deviations from Raoult's law; Raoult's law as a limiting law for unity mole fraction.

Lesson 26 ...boiling point (9) Mole fraction of water in pure water and in a solution. Comparing solutions of sugar and of NaCl at the same molarity. Identifying bp of a solution and bp elevation on a phase map of water. Problem: Calculate bp of a solution made by mixing equal volumes of ethylene glycol (density 1.1 g cm⁻³) and water.

Freezing point

Lesson 27 Introduction (4) How reduced escaping tendency from the liquid phase reduces the freezing point. Identifying fp of solution on a phase map.

Lesson 28 Applications and problems (6)

Freezing point depression constant.

Problem: find the fp of a solution made by mixing 2 volumes of glycol with 8 volumes of water. *Problem:* Estimate the molecular weight of a substance which reduces the freezing point by 0.99 K when 0.49 g is dissolved in 28 g of benzene ($K_f = 5.1 \text{ K kg mol}^{-1}$).

Osmotic pressure

Lesson 29 Osmotic flow ("osmosis") (6) Nature of a semipermeable membrane; operation of an osmotic cell. Dilution of solvent and statistical tendency to maximum disorder as driving force of osmotic flow. Predicting direction of osmotic flow in common examples: candy in mouth, blood cells in water, preserved foods, plants exposed to saline water.

Lesson 30 Osmotic pressure: what is it? (6)

Observation and origin of hydrostatic pressure due to osmotic flow. Measurement of osmotic pressure. Reverse osmosis.

Lesson 31 Osmotic pressure problems (6) The van't Hoff equation and its limitations. *Problems:*

- The osmotic pressure at 25°C of a solution containing 1.43 g of a non-dissociating substance in 140 mL of water is 1.158 atm. Estimate the molecular weight of this species.
- The osmotic pressure at 25° C of a 0.10 M solution of a weak acid HA is 2.7024 atm. Estimate the percent dissociation of this acid.

Mixtures of volatile liquids

Lesson 32 Tutorial on Raoult's law and distillation (11) How the vapor pressure varies with composition; Raoult's law plot for heptane-octane mixture. Estimating v.p. of mixture and composition of its vapor. The vapor is always enriched in the more volatile component; application to formation of "tears" above wine in an open glass. How distillation works.

Lesson 33 Problem: composition of a distillate (4) Two liquids A and B are mixed to form an ideal solution in which the mole fraction of A is 0.40. At 25°C the vapor pressure of pure A is 237 torr and that of pure B is 551 torr. Find the composition of the liquid that can be condensed from the vapor in equilibrium with this solution.

Lesson 34 Solutions that deviate from Raoult's law (3) Meaning of an ideal solution; how differing intermolecular interactions lead to positive and negative deviations from Raoult's law. Estimation of activity coefficient for pesticide residue in puddle.

Solutions of gases in liquids

Lesson 35 Henry's law and the solubility of gases (4) Raoult's and Henry's laws as limiting laws for mole fractions unity and zero; microscopic interpretation; ideal solutions. Henry's law and gas solubility; temperature dependence of Henry's law constant. Applications to transport of O₂ and CO₂ between tissues and atmosphere via the blood, carbonated beverages.

Lesson 36 Oxygen content of water (5)
A problem example.

Lesson 37 Surface properties of liquids (11)

Potential energy of a molecule at the surface, compared to one within the bulk liquid. Tendency to minimize surface area; competing effect of gravity. How insects walk on water: surface tension opposes an increase in surface area. Shapes of drops on wettable and non-wettable surfaces. Water-repellant fabrics, detergents. Capillary flow and its mechanism.

Part 3 - Colloids and surfaces

Lesson 38 Nature of colloids (9) Phases and particles; effect total particle surface area on properties. Surface area increase on subdivision of a cube. Significance of large surface areas; adsorption. Light scattering and the Tyndall effect; the ultramicroscope and brownian motion.

Lesson 39 Types of dispersions (16) Definitions and examples of gels, sols, foams, aerosols, and emulsions.

Lesson 40 Dispersion and coagulation (2)

Lyophilic and lyophobic colloids; the electric double layer. Colloid coagulation as the result of destruction or shrinking of the double layer.

Lesson 41 Surfactants (4) Hydrophilic and amphiphilic solutes; comparison of octane and octanol. Surfactants and detergents. Formation of micelles; ability of micelles to incorporate hydrophobic substances within their internal phase; emulsifying agents. Examples: bile salts in fat digestion, cleansing action of soaps and detergents; lipid bilayer cell membranes.

Part 4 - Crystalline solids

Lesson 42 Long-range order (6) Efficient packing in two dimensions; number of nearest neighbors in square and hexagonal packing. How directed bonds can lead to less efficient packing; example of graphite. The crystal lattice; the unit cell; unit cells for square- and hexagonal packed sheets.

Lesson 43 How identical atoms pack together (9) The cubic crystal system. Simple cubic lattice: number of atoms per unit cell; space lattice, hard sphere, and space-filling representations. Why it is rarely a stable packing arrangement for identical atoms. The body-centered cubic lattice. Close-packed lattices: hexagonal close packing.

Lesson 44 The shapes of crystals (5) How the orderly packing of circles leads to cleavage planes at definite angles between them. Incoming molecules attach to growing crystals at lower-potential energy sites, thereby tending to produce smooth faces. Transformation between cubic and octahedral habits due to selective growth upon certain planes.

4-A. The simplest ionic solids

Lesson 45 How oppositely-charged ions pack together (7) Ionic solids as interpenetrating lattices of oppositely-charged ions. Efficient packing of differently-sized ions places cations in "holes" between close-packed anions. Cubic holes; radius ratio and the CsCl structure.

Lesson 46 Filling the holes: the rock salt and fluorite structures (7) Octahedral holes and the face-centered cubic lattice. Sodium chloride; counting number of formula units in the unit cell. Tetrahedral holes and the cubic-close packed lattice; calcium fluoride.

Lesson 47 Chains, sheets and networks (9) "Infinite molecule" structures as illustrated by CuCl₂, graphite and diamond. Silicates and the silicate minerals: rocks, clays, and quartz.

Chemical Bonding

Why do atoms join together to form compounds, and what determines their structure and stability? Few questions are more fundamental to Chemistry, and in this unit we look at the various models of chemical bonding and learn how to apply them. You will need to master Lessons 1-6 in just about any beginning course, but some of the other topics may be skipped or deferred to later courses, so check with your Instructor to see what is required.

Part 1 - Fundamentals of bonding

Lesson 1 Introduction to Chemical Bonding. Observable properties of chemical bonds. What is a chemical bond? Kinetic and potential energy; potential energy curves and stability in relation to thermal energy; bond energy, bond length, and stretching frequencies; infrared absorption

Lesson 2 Basic theory of the shared-electron bond The H_2^+ molecule; binding and antibinding effects of the electron depending on its location; review of the Uncertainty Principle; bonding as a consequence of electron tunnelling between atoms (This aspect of bonding has not yet made it into most textbooks; you should nevertheless find it interesting and worthwhile).

Lesson 3 Bond polarity and dipole moments Consequences of asymmetric electron distribution in HF. Definition of the dipole moment; simple calculations. Bond polarity and dipole moments in CO_2 , H_2O and CH_4 . Comparison of dipole moments in CH_3Cl , CH_2Cl_2 , and CHCl_3 .

Lesson 4 Polar covalence The Pauling electronegativity scale; electronegativity trends in the Periodic Table. Contrast between electronegativity and electron affinity. Using a table of electronegativities to predict bond polarities. Periodic trends in the halogen halides and in CH_4 , NH_3 , H_2O . Highly-polar and "ionic" bonds; ionic solids.

Lesson 5 The Octet Rule and Lewis electron-dot structures Constructing a theory of valence for C, N, O, and F. The Octet Rule and noble gas structures. The Octet Rule as a natural consequence of energy gaps between *p*- and *d*-block elements. Applications: predicting formulas of molecules and monatomic ions. Bonding and non-bonding electron pairs. Examples: Cl_2 , H_2S , CH_3Cl .

Lesson 6 Multiple bonds and resonance structures Electron-dot structures of CO_2 , CO , C_2H_6 , C_2H_4 , and C_2H_2 . Comparison of C-C bond lengths in the latter three compounds. Equivalent structures and bond orders in SO_2 , and SO_3 ; comparison with SO_3^{2-} . Bond order in the NO_3^- ion.

Lesson 7 Formal charge Formal charges in NH_4^+ , H_2O . Assessing the relative importance of different bonding arrangements in NO and SCN^- .

Part 2 - Part 2 - Shapes of molecules

Lesson 8 Introduction to VSEPR theory Orbital repulsion, axial and equatorial positions in octahedral structures.

Lesson 9 Tetrahedral coordination Distinction between coordination and molecular geometry when non-bonding electrons are present.

Lesson 10 Higher coordinations Octahedral and trigonal bipyramidal coordination.

Lesson 11 Drill exercise Ten examples randomly selected from 13, covering all major shapes.

Part 3 - Hybrid Atomic Orbital model of chemical bonding

Some introductory courses will treat hybridization fairly lightly, if at all. If you plan to take a course in organic chemistry, the first three topics in this section will be important to you.

Lesson 12 Introduction How to think about hybrid orbitals. Inadequacy of *s*- and *p*- atomic orbitals in explaining bonding in CH_4 ; sp^3 hybrids as a more useful set of equivalent orbitals. Analogy with standing waves; in-phase and out-of-phase combinations of *s*- and *p*-orbitals; shapes of the resulting hybrids.

Lesson 13 Single bonds General principles of constructing and predicting shapes of hybrid orbitals. CH_4 , BF_3 , BeH_2 .

Lesson 14 Multiple bonds Ethane, ethylene and acetylene; role of atomic-*p* orbitals; σ - and π - orbitals. "Bent-bond" model as an alternative approach to multiple bonding. Hybrid orbital description of the nitrate ion.

Lesson 15 Hybrids involving *d*-orbitals Non-bonding electrons in hybrid orbitals; examples of NH_3 , H_2O , NO_3^- , $[\text{PtCl}_4]^{2-}$, PCl_3 and PCl_5 , SF_6 , $\text{Zn}(\text{NH}_3)_6^{2+}$ and coordinate covalent bonds; configuration of Fe(III); inner- and outer- transition metal complexes. The magnetic balance.

Part 4 - Molecular Orbitals

Check with your instructor to find out how much, if any, of this subject you are expected to know; some introductory courses leave it out entirely. If you do cover the molecular orbital model of bonding, this group of lessons treats the subject at the level commonly required in first-year courses. The major objective is to make you able to predict the bond orders in diatomic molecules of the first- and second-row elements. An introductory lesson develops the basic idea of the splitting of atomic orbitals into bonding and antibonding pairs. The final two topics are the most interesting ones but are often skipped in beginning courses.

Lesson 16 Introduction Attractive and repulsive forces in the simplest molecule, H_2^+ . Identifying in- and out-of-phase combinations of hydrogen *1s* wave functions, and bonding/antibonding orbitals.

Lesson 17 Simple m.o.'s from atomic-*s* orbitals Bond orders and relative bond energies of H_2 and H_2^+ . Working out orbital occupancies and bond orders in He_2 , He_2^+ , Li_2 , Be_2 , LiH . Review based on Li and Be .

Lesson 18 Survey of second-row homonuclear diatomics B_2 , C_2 , N_2 and its cation and anion, O_2 , and F_2 .

Lesson 19 Transition metal ions Shapes of *d* orbitals; identifying those most strongly affected by an octahedral field. Consequences of ligand field splitting.

Lesson 20 Metals and semiconductors Qualitative introduction to band theory of metals and semiconductors. Molecular orbitals in Li_2 , Li_3 , and Li_4 ; splitting into filled and unfilled levels; extension to Li_n . Mechanism of electrical and thermal conduction by excitation of electrons to contiguous unoccupied levels. Overlap of *2s* and *2p* bands in Group 2 metals, development of band gap within periods; semiconductors. Temperature coefficient of conductivity in semiconductors; insulators.

Fundamental concepts of acid-base chemistry

This is the first of two lesson sets on this very important subject. The reason for splitting them up this way is to accommodate students in courses in which a “light” treatment of acid-base chemistry is offered in the first semester, followed by a more thorough treatment (usually emphasizing calculations) in a later course. Other courses and many textbooks combine all this into a single unit. If this is the case for you, beware of the frequent practice of placing so much emphasis on calculations that the fundamental concepts never get properly developed. In other words, you should try to go through *everything* in this lesson set, whether or not it is a part of your official course syllabus. This should not be difficult to do; except for the section on pH, where you will need some knowledge of logarithms, this lesson set is refreshingly math-free.

Lesson 1 Introduction (12) Properties of acids and bases; taste, touch, neutralization. Definition of an acid; role of O and H; Arrhenius theory of acids and bases. The hydrogen ion: size and charge density. The hydronium ion.

Proton ping-pong

Lesson 2 Proton donor-acceptor theory of acids and bases (12) Brønsted definition of acids and bases; conjugate species. The role of water. Dissociation of HCl; water as the default base. Acidic character of ammonia; the conjugate base.

Lesson 3 Polyprotic and amphiprotic acid-base systems (12) Identifying conjugate species in various acid-base reactions. Amphiprotic species; HCO_3^- ; HSO_3^- , sulfate and ammonia series. Reactions of ampholytes with themselves. Water and the $\text{H}_3\text{O}^+/\text{OH}^-$ series.

Fall of the proton

Lesson 4 The proton ladder (11) Review of proton and hydronium ion. Acid-base chemistry as a contest; the weaker acid wins the proton. Cl^- vs. water. The proton energy scale; placing substances on the proton ladder: HCl, H_2O , HClO_4 . Comparison of HCl and HClO_4 solutions; the leveling effect. H_3O^+ as the strongest acid that can exist in aqueous solution (See the figure on the following page.)

Lesson 5 Reactions between weak acids and bases (23) Energetics of the dissociation of a weak acid in water; role of thermal excitation. Competition between bases; partial neutralization of a mixture of bases by HCl; “the weak shall inherit the proton”.

Using the proton ladder to predict directions of NH_3 -phenol and $\text{NH}_3\text{-HSO}_4^-$ reactions. Use of OH^- to ensure quantitative reaction. Energetics of water autoprotolysis. Bases stronger than OH^- ; oxide and amide ions. Relative acid-base strengths in liquid ammonia, comparing extents of autoprotolysis in H_2O and NH_3 .

Recognizing common acids and bases

Lesson 6 M-H compounds (7) Acidic and basic hydrides; periodic trends; effects of Z and size. Identification of strongest/weakest acids.

Lesson 7 M-OH compounds (10) Acid/base character of M-O-H for metal and nonmetal M. Oxyacids; comparison of MOH, $\text{MO}(\text{OH})$ etc. Examples: CH_3OH - H_2CO_3 , HNO_2 - HNO_3 . The chlorine oxyacids. Alkaline -OH compounds. Acid-base character of oxides; acid anhydrides.

Lesson 8 Hydrated metal ions (2) H_2O as source of acidity in FeCl_3 solutions; effect of central ion charge.

Lesson 9 Salts (6) Example of NaOCl; its reaction products with H_2O ; hydrolysis. Extent of hydrolysis reactions. Comparison of ClO^- and Cl^- as bases in water. Hydrolysis of NH_4^+ .

Lesson 10 Organic acids and bases (8) (In two parts, a tutorial and quiz. Option is given to skip directly to quiz.) Functional groups. The carboxyl group; reason for its acidity. Effect of nearby atoms on acid strength; the chloroacetic acids. Phenol as an acid. The amino group; methylamine and aniline.

Lesson 11 Reactions of acids and bases (22) Formation of salts; writing net ionic equations and estimating extent; reactions of strong and weak acids

and bases. Controlling direction of reaction by allowing escape of gaseous components; reactions of carbonates with acids. Reactions of conjugate forms of ampholytes. Reactions of metals with acids and bases.

The pH scale

Lesson 12 The ion product of water (4) The value of K_w and of $[H^+]$ or $[OH^-]$ in aqueous solutions.

Lesson 13 The pH scale (6) Review of ion product. Benefits of a logarithmic scale. Definition of pH, pOH, pK_w ; the relations between these quantities. The distinction between analytical and effective concentrations; pH as a measure of the availability of protons in the solution.

Lesson 14 pH calculations (8) pH of solutions of strong acids and bases; changes in pH resulting from dilution.

Lesson 15 pH of common substances (7)

Seawater, blood, gastric fluid, lemon juice, rainwater, NH_3 solution, $NaHCO_3$ solution.

Acid-base titration

Lesson 16 What we measure (7) Titrant and the burette; concentrations. Calculating the number of moles.

Lesson 17 The reactions (12) Need for quantitative reactions; assessment of several cases. End point and equivalence point. Writing ionic equations for titrations involving strong and weak acids. Nature of solution at the equivalence point.

Lesson 18 Titration curves (18) What we plot. Estimating pH of equivalence point and pK of acid from the titration curve. Comparison of curves for acids of different strengths. Buffering at low and high pH; its effect on the curve. Curves in which equivalence point breaks are not seen; H_2SO_4 , H_3PO_4 ; titration curves of sulfurous acid and succinic acid.

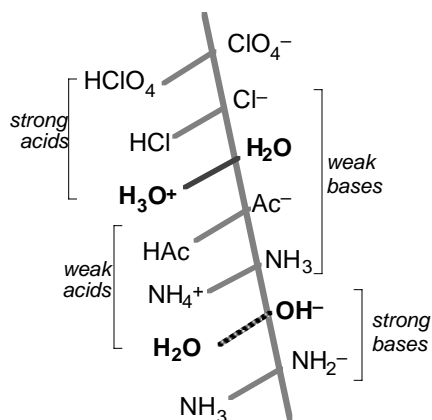
Lesson 19 Detecting the equivalence point

(8) From titration curve second derivative and by indicator. Color of indicator at its pK . Relation of pK of indicator to that of the substance being titrated. Selecting an indicator for a given titration.

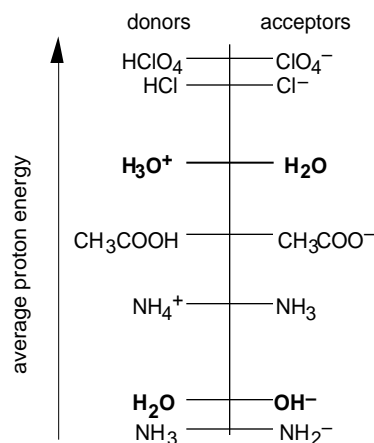
Acid-base drill exercises

Lesson 20 Acid names drill (Formula of acid is given, student selects name from list.)

Lesson 21 ABN drill (Is the solution acidic, basic, or neutral?)



The concept of the “proton ladder” is developed in Lesson 4 as an aid to understanding acid-base reactions such as those introduced in Lesson 5. This modern view of acid-base chemistry has still not worked its way into most present-day textbooks, which is a shame because it helps you to visualize and understand acid-base reactions without memorizing a lot of detail or doing quantitative calculations. We strongly recommend that you go through these two units, no matter what course you are taking.



Acid-base equilibria and calculations

This is a continuation of the previous unit on acid-base concepts. All of these lessons presuppose some familiarity with equilibrium constants and their use. There is probably more material in this lesson set than you will need in any single course, so it will be wise to seek guidance from your instructor. In any case we strongly recommend that you do Lessons 3-5; it will provide you with a far better understanding of acid-base systems without the obfuscation that the standard textbook treatment entails. If you love to do algebra, avoid Lessons 21-22. Lessons 27 through 33 will probably be more useful to students in analytical or environmental chemistry courses.

Introduction to acid-base equilibria

Lesson 1 Acid-base strength (9). Competition for protons; value of K for $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$. Meaning of acid and base strengths; defining K_a and K_b . Acid-base reactions: “*the weak shall inherit the proton*”. Relations between the acid and base constants of conjugate species.

Lesson 2 Equilibrium constants of acid-base reactions (8) K_a values and the proton ladder; using pK information to predict the outcome of acid-base reactions. Comparing K 's for reaction of a weak acid with a weak base and with hydroxide ion; reaction of a strong acid with OH^- , and of a weak base with water (hydrolysis).

How the pH controls the composition

Lesson 3 Introduction: α distribution plots. (9) Effect of pH on concentration ratio of acid and base forms of a conjugate pair; pH as a controlling variable. Definition of the alpha concentration fractions; identifying plots of α_0 and α_1 ; relation to pK . Conversion between concentration ratios and alpha's.

Lesson 4 Pushing protons up the ladder (5) The pH as a measure of average proton energy (see Fig. 3 on page 3.)

Lesson 5 It's all a plot! (15) Log-concentration vs. pH plots. Development of the plot; graphing H^+ and OH^- , and of HOCl and OCl^- for a hypochlorous acid solution (see Fig. 3 on page 4.)

Lesson 6 Solutions of strong acids (11) Construction of a pH vs. log- C diagram for HCl , showing linear, curved, and zero-slope parts of the plot. Development of charge-balance and mass-balance equations, and of the exact equation for $[\text{H}^+]$ in a strong acid; simplifying this equation. Finding the concentration at which the error of not using the exact equation is 10%.

Monoprotic weak acid calculations

Lesson 7 Exact treatment (5) Number of species to deal with, and the relations between them; K_a , K_w , charge balance and mass balance. The exact (cubic) equation for $[\text{H}^+]$; its simplification to a quadratic.

Lesson 8 Quadratic approximation (5) Setting up the expression for K_a . Substituting $[\text{H}^+]$ for $[\text{A}^-]$ and $(C-[\text{H}^+])$ for $[\text{HA}]$. Expressing this in standard polynomial form; value of a and b coefficients.

Lesson 9 Square root approximation (9) Simplifying the K_a expression by substituting $[\text{H}^+]$ for $[\text{A}^-]$ and C for $(C-[\text{H}^+])$. Judging the validity of this approximation for 0.1M and 10^{-5} M solutions of various weak acids.

Lesson 10 Example: HNO_2 (4) Comparison of two approaches: Setting up quadratic expression, testing to see if it can be simplified, evaluating polynomial coefficients, selecting the correct root from a plot of the polynomial.

Buffer solutions

Lesson 11 Introduction (13) Writing the Henderson-Hasselbalch equation; distinction between $[\text{HA}]/[\text{A}^-]$ and C_a/C_b . Designing buffer solutions; concentration and K_a considerations. Making buffers by directly combining conjugate pairs, and by partially neutralizing the pure weak acid or base; examples for acetate and borate buffer systems.

Lesson 12 How buffers work. (9) How small additions or removals of H^+ or OH^- ions make only small changes to the C_a/C_b ratio; detailed example for .015 M acetate buffer.

Lesson 13 Why they sometimes don't work. (8) Effects of buffer concentration; examples for acetate buffers of 0.15 and .0015 M.

Lesson 14 Beyond the Henderson-Hasselbalch equation (6) Limitations and misapplication of the H-H equation. Derivation of the exact relation between $[H^+]$ and the C_a/C_b ratio; simplification to a quadratic, and the conditions under which this may be used.

Bases, salts, and hydrolysis

Lesson 15 Calculations involving weak bases K_b and the relation between K_a and K_b (3)

Lesson 16 Solving for $[OH^-]$ (7) Development of the exact expression for $[OH^-]$ in a solution of a weak base; simplifying approximations.

Lesson 17 Example Problem (9) Find the pH of a .01M solution of methylamine in water. Solution of quadratic by trial-and-error.

Lesson 18 Salts: Introduction (9) Why salts of weak acids give alkaline solutions; hydrolysis. Example of NaOCl; placement of HOCl on proton ladder diagram; small magnitude of hydrolysis equilibria. Evaluating the equilibrium constant.

Lesson 19 Example: NaCN (6) Calculation of pH and percent hydrolysis of a .01M NaCN solution

Lesson 20 Example: Na_2SO_4 solution (5) Illustrating the failure of the usual approximations and the need for the exact (cubic) expression, which is solved by iteration.

Graphical methods of calculation

Lesson 21 Review of log-C plots (15)
(Same as Lesson 5)

Lesson 22 Estimating the pH (12) Proton balance; using log-C plots to estimate pH of a solution of a weak acid and of its conjugate base; HOCl example problem. See Fig. 3 on page 4.

Lesson 23 Ammonium formate (5) A more complicated example: a salt of a weak acid *and* a weak base.

Lesson 24 Relation between log-C plot and titration curve. (6) Example for HOCl; picking system points for solution at titration fractions 0, 0.5, and 1.0.

Polyprotic systems

Lesson 25 Introduction and overview (15) Relation between K_1 and K_2 and their ratio in various diprotic acids; H_2S , H_2SO_4 , $HOOC-(CH_2)_n-COOH$, oxyacids. Distribution (*alpha*) plots for diprotic acids; identifying pK and pH of equivalence point.

How closer pK 's limit the maximum ampholyte fraction. Polyprotic bases, amino acids; zwitterions and their migration in an electric field.

Lesson 26 Finding the pH and composition of diprotic acid solutions (10) A 0.01M solution of oxalic acid is used as an example. Development of an approximate expression for $[H^+]$, and its solution by iteration. Comparison with exact solution taking into account the second dissociation step. Use of a log-C diagram to estimate the pH of solutions of H_2Ox , $NaHOx$, and Na_2Ox .

Lesson 27 Phosphate species distribution and pH (6) Log-C diagram for a triprotic system; estimating the pH of solutions of H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 .

Lesson 28 Phosphate buffers and mixtures (13) Calculating the phosphate species ratio for buffer of a given pH; distinction between ratio and fraction. Making this buffer from H_3PO_4 and NaOH, and from Na_3PO_4 and HCl. Proton transfer between phosphate species; compatible and incompatible combinations; predicting the composition of mixed phosphate systems. Calculation of K . How the predominant species resulting from mixing H_3PO_4 and Na_3PO_4 will depend on the relative quantities.

Carbonates and natural waters

Note: Most of the following lessons presume an understanding of log-C vs. pH plots as developed in Lessons 21-22.

Lesson 29 Introduction: why is this important? (4) Overview of the carbonate system; carbonates in natural waters and in the blood; the geochemical carbon cycle.

Lesson 30 pH and carbonate species distributions (9) Development and interpretation of log-C vs pH plots for solutions of CO_2 , $NaHCO_3$ and Na_2CO_3 .

Lesson 31 pH of carbonate solutions (7) Using log-C plots to estimate the pH of solutions of CO_2 , $NaHCO_3$ and Na_2CO_3 at concentrations of .001M and 1E-5M. Effect of photosynthesis on the pH of natural waters. Open and closed systems.

Lesson 32 Carbonate titrations 1 (4) The CO_2 titration curve; simple acidity titrations.

Lesson 33 Carbonate titrations 2 (9) Alkalinity titrations; determination of multiple carbonate species in natural waters.

Appendix: Reference diagrams for users of Part 2 lessons

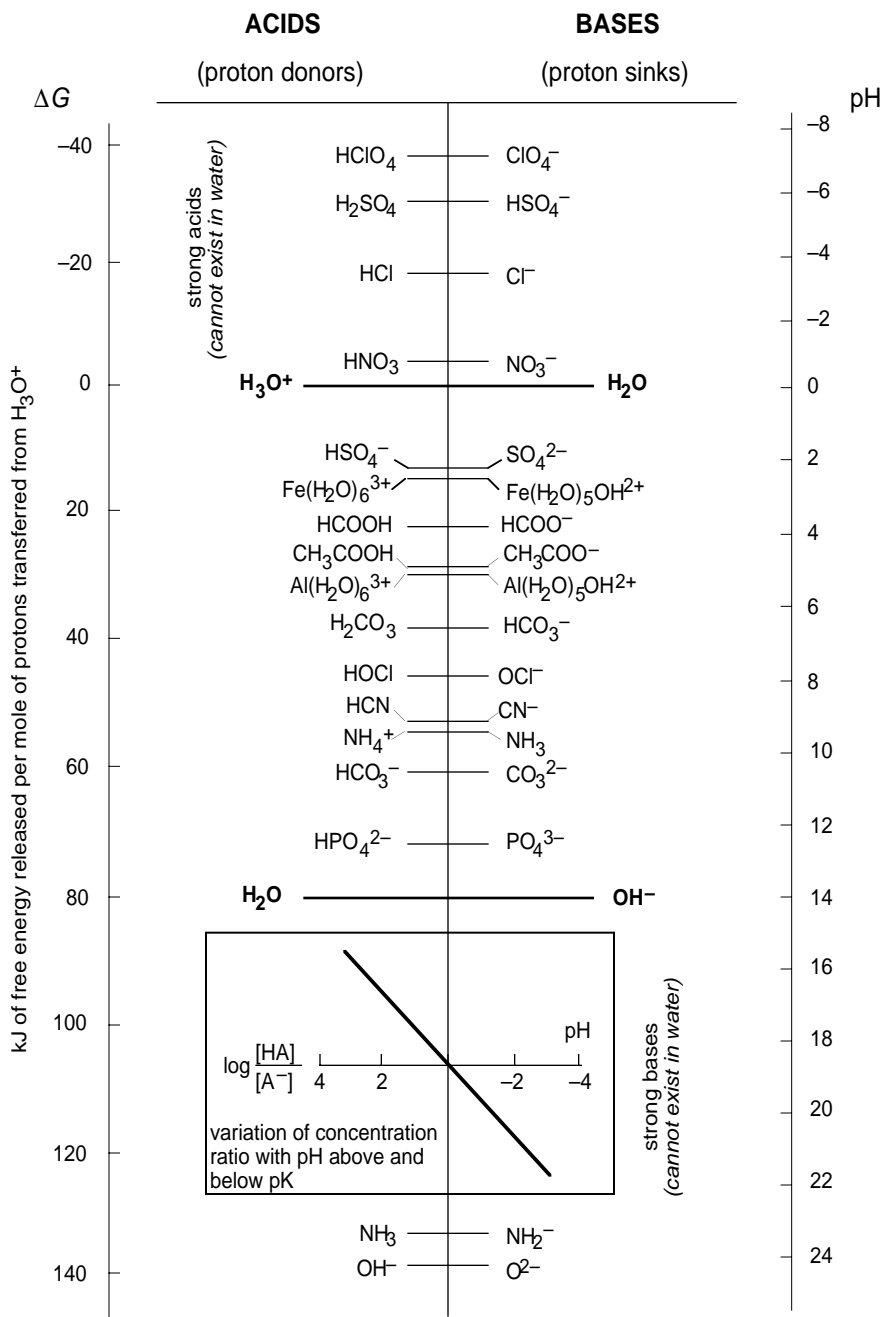


Fig. 1 Proton free energy diagram (Lesson 6) This shows how the average free energy per mole of protons depends on the pH. The height of each conjugate pair indicates the pH at which it is half-protonated, and thus its pK_a . An acid-base reaction corresponds to the transfer of a proton from a source to a sink; if the latter is at a higher energy, the reaction is incomplete. This is the case for all acids weaker than H_3O^+ (the strongest acid that can exist in water). The inset near the bottom shows how the pH deviates from the pK_a when the ratio of acid to base deviates from unity.

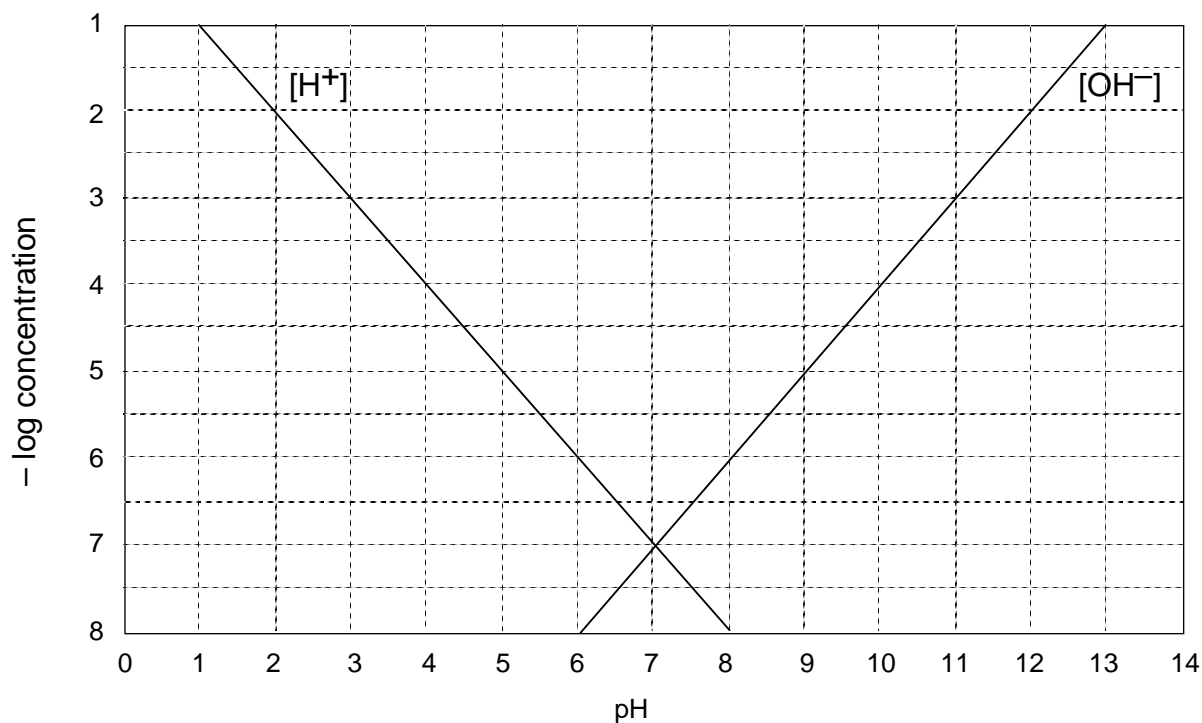


Fig. 2 Use this diagram as a template to construct log-concentration vs. pH diagrams of the kind described in lessons 5 and 22.

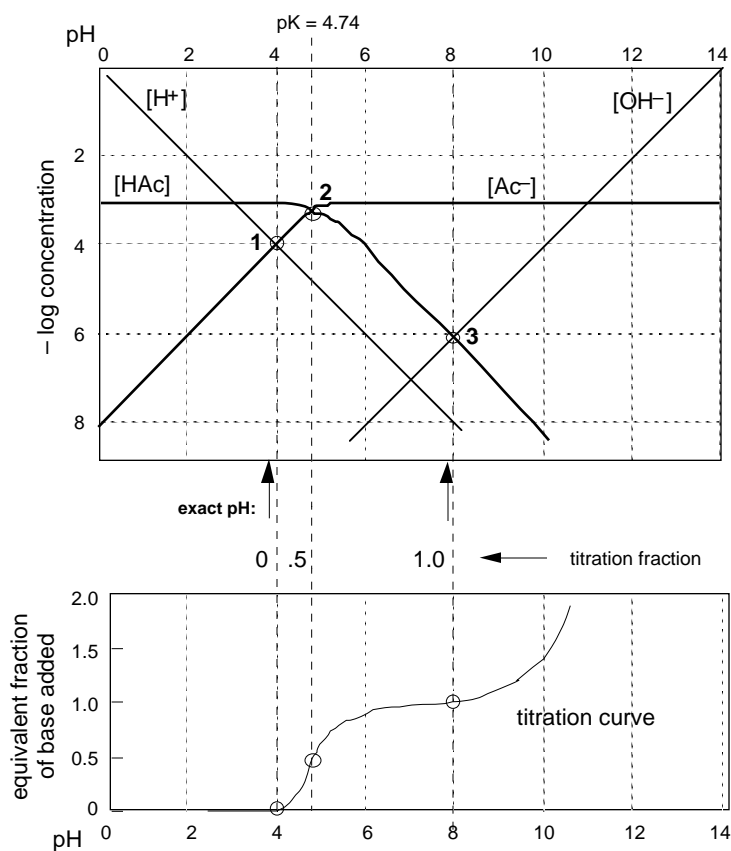


Fig. 3 Log-C-pH diagram for 10^{-3}M acetic acid. The pK_a of the acid and its nominal concentration C_a uniquely determine the appearance of the plots. Beyond the values of these two quantities, only one other number is required: the value -0.3 ($\log 0.5$.) This represents the crossing point **2** of the plots for $[\text{HA}]$ and $[\text{A}^-]$, since when $\text{pH} = pK_a$, $[\text{HA}] = [\text{A}^-] = 0.5 C_a$. Except for a small region near the pK_a , the slopes of the two plots are either zero, or ± 1 (this is easily proved.)

Point **1** represents the concentration condition $[\text{H}^+] = [\text{A}^-]$ produced by the reaction $\text{HA} \rightarrow \text{H}^+ + \text{A}^-$. and this establishes the pH (4.0) of a solution of 10^{-3}M HAC in pure water..

For a solution of the conjugate base NaA, the hydrolysis reaction $\text{A}^- + \text{H}_2\text{O} \rightarrow \text{HAc}$ establishes the condition $[\text{HA}] = [\text{OH}^-]$ corresponding to the intersection **3** of these two plots, which occurs at pH 8.0. As the arrows at the bottom of *a* indicate, these pH values are within 0.1 pH unit of what an exact calculation would predict.

The bottom diagram shows how the titration curve of the acid relates to the log-C vs pH plot. (See lesson 22.)

Chemical Equilibrium

The lessons in this group introduce the concept of equilibrium at an elementary level, and go on to describe the LeChâtelier principle, the equilibrium quotient Q , and the equilibrium constants K_c and K_p . Most of this will be suitable for all levels of General Chemistry. The section on equilibrium calculations is a bit more advanced, and might well be skipped by students in “prep” courses. The problem exercises in this section illustrate the use of iterative approximation and graphic calculations to solve quadratic equations.

Please note that certain special types of equilibria such as acid-base, oxidation-reduction and solubility are not covered in this lesson set.

Lesson 1 Introduction to chemical equilibrium (16) Definition of equilibrium, reversible reactions; HI synthesis as example of an incomplete reaction; identifying equilibrium state on conc'n-vs-time plot; reversibility; dynamic nature of equilibrium with forward and reverse rates identical; Law of Mass Action. Criteria for equilibrium; examples judged against these criteria. Finding extent of reaction in $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ example. Comparing reaction rates from plots of conc'ns vs. time; catalysts.

Lesson 2 LeChâtelier Principle (8) Shifts in composition resulting from non-identity of forward and reverse rates; how adding more reactant can bring this about; effects on conc'n-time plot for HI synthesis. LeChâtelier principle; using it to predict effects of changes in various reaction systems.

Lesson 3 Equilibrium expressions: Q and K (8) Extent of reaction; the equilibrium quotient Q , writing equilibrium expressions. The equilibrium constant K as a special case of Q . How ratio Q/K affects “shift” of reaction to right or left.

Lesson 4 More on equilibrium expressions (17) Dealing with unchanging concentrations. Reactions in aqueous solution involving water; molar concentration of pure water. Definition of a heterogeneous reaction; example of thermal decomposition of CaCO_3 . Hydrates; K_p for decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from its vapor pressure. Vapor pressure of water and its equilibrium constant; [non]-influence of liquid volume. Finding K_p from vapor pressure table; value of K_p at boiling point. Condition at which vapor pressures of water and ice are identical. Relative humidity produced by $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in a closed container.

Equilibrium Calculations

This section is presented as a series of guided problem exercises that are intended to illustrate various aspects of equilibrium calculations.

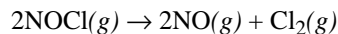
Lesson 5 K_p for the dissociation of a solid (2).

Solid ammonium hydrosulfide dissociates according to $\text{NH}_4\text{HS}(s) \rightarrow \text{NH}_3(g) + \text{H}_2\text{S}(g)$.

If the total gas pressure in a sealed container of ammonium hydrosulfide is $\overline{280}$ torr, find the value of K_p at this temperature.

Lesson 6 Dissociation of nitrosyl chloride (8).

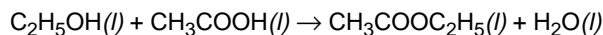
Nitrosyl chloride is an orange gas that dissociates at high temperatures into chlorine and nitric oxide:



In a certain experiment, $\bar{2}.0$ moles of NO, $\bar{3}.0$ moles of Cl_2 , and $\bar{1}.4$ moles of NOCl were introduced into a 10 liter container.

- What is the value of the equilibrium quotient Q_c under these conditions?
- After equilibrium was reached, there were $\bar{3}.2$ moles of NOCl in the container. Use this information to evaluate Q_c and the equilibrium constant K_c .

K_c for Formation of an ester. The next two lessons refer to the reaction



Lesson 7 K from equilibrium composition (3) When 1 mole of ethanol reacts with 1 mole of acetic acid, the equilibrium mixture consists of $\bar{3}/\bar{7}$ mole each of water and the ester, ethyl acetate. Use this information to evaluate K_c .

Lesson 8 Equilibrium composition from K_c (5)

Calculate the equilibrium composition after $\bar{2}$ mol of alcohol and $\bar{5}$ mol of acid have been combined if $K_c = \bar{4}$.

Lesson 9 Percent dissociation of PCl_5 (5)

If $K_p = 1.78$ at 250°C , calculate the percentage of PCl_5 that will be dissociated when $0.0\bar{7}$ mol of PCl_5 is placed in a closed vessel at 250°C and the total pressure at equilibrium is 2 atm.

Chemical Energetics

The lessons in this set provide a comprehensive introduction to the role that energy plays in Chemistry; they constitute a more complete development of some of the material introduced in the *Energy, temperature and heat capacity* section of the CB01 *Square-1* lesson set. These lessons break the subject up into smaller bits that we hope you will find more readily digestible than the treatments offered in many of the current textbooks. Some courses do not cover the material in Lessons 6-9, so you should check with the course outline or with the instructor before putting much effort into these.

Lesson 1 What thermodynamics is all about (6)

Definition and purpose; system, surroundings; state of a system, state variables; composition as a state variable; the equilibrium composition.

Lesson 2 Chemical energy: how molecules absorb and store it (20)

Potential energy and kinetic energy; translational, vibrational and rotational modes; temperature and heat capacity; contributions of the various modes to the heat capacity. Monatomic and diatomic molecules. Observed heat capacities of polyatomic molecules; C vs. T plot for dihydrogen, effect of quantization of energy levels. Heat capacity and molecular complexity.

Lesson 3 Heat and work: how to tell them apart; the First Law (11)

Endothermic and exothermic processes; sign convention for enthalpy change; delta-notation. Definition of work; work accompanying vaporization of H_2O ; internal energy, work, and enthalpy; statement of the First Law; relation of ΔU and ΔH to q_v and q_p .

Lesson 4 How the internal energy and enthalpy change with temperature (15)

Units of heat capacity. Constant-volume and constant-pressure heat capacities. Relation of C_v and C_p to ΔU and ΔH . Molar and specific heat capacities. Heat capacity- and enthalpy vs. temperature plots for water; heat effects associated with phase changes. Heating and cooling curves. The large heat capacity of water; effect on coastal climates.

Lesson 5 Chemistry and the First Law: heat and work in chemical reactions

Summary of the First Law. Estimating the work, and thus ΔU in several chemical processes: dissolution of $\text{HCl}(g)$; Calcination of $\text{CaCO}_3(s)$, $\text{Zn} + \text{HCl}$.

Lesson 6 Paths and cycles; more on the First Law (11)

Nature of isothermal processes. Heat absorbed in constant-pressure isothermal expansion, and in a constant-volume heating of the gas. Tracing isothermal, isopiestic and isochoric changes on a PVT surface. Visualization of a closed cycle and zero net changes in state functions. Constructing equivalent paths to calculate changes that occur at neither constant P nor constant V .

Lesson 7 Turning off the heat; adiabatic processes (7)

Contrast between an isothermal and adiabatic compression; adiabats on a P - V plot.

Lesson 8 Reversible and irreversible processes (12)

Calculation of work in single- and two-stage expansions of an ideal gas; extrapolation to infinite number of stages. Contrast with compressions. Representation as areas on P - V plots. Definition and significance of a reversible process.

Lesson 9 Summary of the first law

Lesson 10 Heats of reaction: enthalpy and Hess' Law (8)

Relative enthalpies of CO_2 and of its elements; the "zero" of chemical enthalpies; calculation of enthalpy of combustion of carbon monoxide. Hess' law and its application to finding the heat of formation of methane from heat of combustion data.

Lesson 11 Using standard enthalpies of formation (16)

Using tables of standard enthalpies of formation: heat of combustion of carbon, combustion of carbon monoxide and of dihydrogen. Enthalpy of vaporization of water. Enthalpy of hydrogenation of ethylene. Formation of benzene from acetylene, atomization of dioxygen, enthalpy of the H-H bond; comparison of homonuclear bond energies.

Ionic enthalpies; H^+ as basis. Standard enthalpy of formation of Cl^- from that of $\text{HCl}(aq)$. Use of table of ionic enthalpies to estimate heat of neutralization, heat of dissolution of $\text{NaCl}(s)$.

Lesson 12 Bond enthalpies (6)

Average C-H bond energy in CH_4 ; use of table of standard enthalpies of formation to estimate the heat of atomization of ethylene, and thence of the C-C double bond. Use of table of bond enthalpies to estimate the enthalpy of the reaction $\text{CH}_4 + \text{F}_2 \rightarrow \text{CH}_2\text{F}_2 + \text{H}_2$.

Lesson 13 Calorimetry (8)

Measuring heat by temperature change of water; examples of drop calorimeter, solution calorimeter and bomb calorimeter for heat of combustion; observation of internal energy vs. enthalpy change.

Electrochemistry

You will find somewhat more detail in these lessons than what is presented in most introductory courses, which tend to treat electrochemistry rather superficially, often going little beyond teaching you how to draw pictures of cells and to set up and use the Nernst equation. In most conventionally-taught courses there is simply not enough time to take the class through the details required to develop a thorough understanding of the subject even at the elementary level.

These lessons place a great deal of emphasis on developing the fundamental concepts, and in linking them with applications such as corrosion, membrane potentials and potentiometry. Although they are intended primarily for use in a General Chemistry course, the electrochemistry lessons should also serve as a review and a basis for further work in more advanced courses in analytical and physical chemistry.

Part 1 - Basic principles

Lesson 1 Introduction: redox reactions, electrodes and cells (11). What happens when a piece of zinc metal is immersed in water: how separation of charges inhibits the dissolution of Zn^{2+} ions, and how this can be overcome by providing a second piece of Zn immersed in a Zn^{2+} solution. Concentration effects discussed in terms of the LeChâtelier principle. The need to provide a path for ion migration between the two half-cells.

Lesson 2 The activity series: the fall of the electron (12) We now immerse a piece of zinc in a Cu^{2+} solution; what product is formed, and what does this tell us about the relative electron-accepting powers of Cu^{2+} and Zn^{2+} ? A similar experiment using Ni and Ni^{2+} solutions allows us to place these three cations on a scale of electron-accepting ability. Placement of H^+ on this scale; expanding it to a list of electron sources and sinks. Drill on using the activity series scale to predict the direction of a variety of redox reactions.

Lesson 3 Standard electrode potentials (9) Electron flow direction and potential difference in a Ag/Ni cell; replacing the Ni^{2+}/Ni electrode with others that produce greater potential differences. PD as a measure of tendency for reaction to occur. H^+/H_2 couple as the basis for comparisons; the hydrogen electrode and standard electrode potentials. Using standard EMFs to predict electron flow direction in the external circuit.

Lesson 4 Using half-cell EMFs (9) How to use standard half-cell potentials to determine the potential of a complete cell. Cell notation: the convention for depicting reduction on the right. Cells involving Ag/AgCl and Pt/ $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrodes.

Lesson 5 Electrolytic cells (15) Review of electron flow in spontaneous operation of a galvanic cell. Value of externally-applied potential required to stop the reaction, and to drive the reaction in reverse. Construction and operation of an electrolytic cell; example of NiCl_2 ; calculation of amount of Ni deposited given time and current. Cathodic and anodic products in electrolysis of NaCl, NaNO_3 .

Lesson 6 Electrochemical corrosion (16) Requirement for electron acceptor or depolarizer; H^+ and O_2 as the most important; how contact with a more noble metal can also lead to corrosion. Details of electron flow and metal dissolution in a corrosion cell. Corrosion protection by noble and sacrificial coatings, and by externally-applied cathodic protection. Anodic sites produced by stress. pH change associated with O_2 -induced corrosion; rusting of iron. Oxygen deprivation and pitting corrosion. Protection by passivation in stainless steel, adherent oxide films in Al.

Lesson 7 Thermodynamics of electrochemical cells (16) System and surroundings in a cell; the external circuit as part of the surroundings. Nature of electrical work; calculation of work for 1 mole of reaction. How the work varies with the resistance in the external circuit; condition for maximum work, identification with free energy change. Example of the cell $\text{Zn} | \text{H}^+ || \text{H}^+ | \text{H}_2$; calculation of heat and work in reversible operation; how the heat changes when cell operates irreversibly. Cell potential as free energy per electron-mole. Example of $\text{Ni} | \text{Ni}^{2+} || \text{Ag}^+ | \text{Ag}$; relation of E° and nFE° values for half reactions and net reaction. Entropy change and temperature dependence of E .

Part 2 - The Nernst Equation and its applications

Lesson 8 Nernst Equation (21) How the free energy and cell potential change with concentration (LeChâtelier); The Nernst Equation. Plots of E vs. $\log-C$ for mono- and divalent ions. Estimating E for dilute solutions against SHE. Effect of ion activities. Estimating activity coefficient. Constructing Nernst equation and calculating E° for a couple. Adjusting the ion activity to make $E = E^\circ$. Meaning of E° in terms of H_2/H^+ and the SHE. Extent of dilution required to reverse current flow. The Fe^{3+}/Fe^{2+} couple; using E as master variable to control the ion concentrations. Value of E to bring reaction to equilibrium, and to make $\{Fe^{2+}\} = \{Fe^{3+}\}$. $\log-C$ vs. E_h plot for Fe^{3+}/Fe^{2+} system.

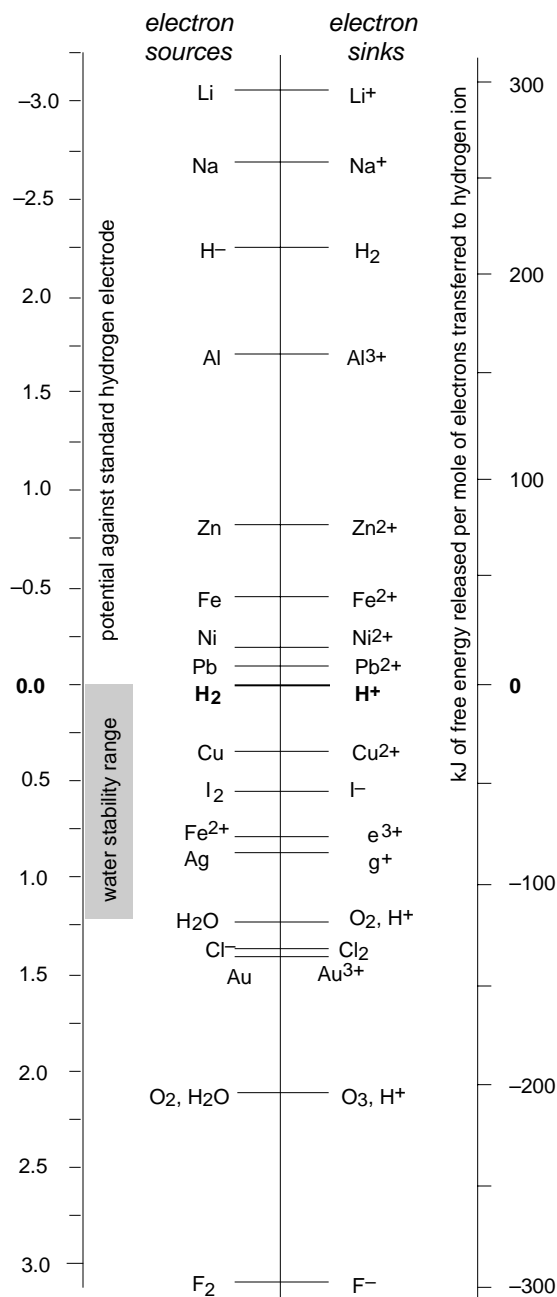
Lesson 9 Concentration Cells (8) How a concentration difference leads to a free energy difference; E° of a concentration cell is always zero. Spontaneous direction and potential difference of a concentration cell. Special case of zero- and one-ion per litre concentrations on one side; unpoised electrodes. Membrane potentials: their origin and sign.

Lesson 10 pH Measurement (5) The pH that corresponds to unit H^+ activity; construction of the standard hydrogen electrode; estimating the potential against a solution of a given pH. $Ag/AgCl$ reference electrode; estimating its potential difference. The glass electrode.

Lesson 11 Measuring solubility and formation constants (8) Silver-ammonia complex ion; electron flow in a cell $Ag^+ | Ag^+, NH_3$; effect of complexing on half-cell potential. Using measured potential to evaluate the formation constant. Construction of a cell whose net reaction is the dissolution of a salt.

Lesson 12 Potentiometric titrations (7)

Example of Fe^{2+} concentration measurement by oxidation to Fe^{3+} . Selection of a suitable oxidant; use of Ce^{2+} . Construction of a suitable titration cell. Analysis of cell potential in terms of the Nernst equations for oxidant and reductant; how the potential is undefined at the equivalence point. Shape of the titration curve.



The above diagram, which is developed in Lesson 2, shows the energy levels to which electrons can “fall” in the presence of the various oxidizing agents shown on the right side. The scale on the left shows the corresponding standard cell potentials. Although you still need a table of electrode potentials for quantitative calculations, this kind of diagram makes it far easier to visualize the relations between different oxidizing and reducing agents.

Chem1 Concept Builder provides guided, interactive and *in-depth* instruction in General Chemistry at the college and advanced-high school levels. It is especially suitable for courses in which the computer plays a major role in the delivery of instruction, in distance education, and for independent study, but it can also serve as a useful supplement for traditional instruction and as a source of review for students preparing for advanced courses in analytical chemistry, environmental chemistry, and biochemistry.

There are more than 150 lessons, each individually accessible through a series of hierarchical menus. A typical lesson involves between 12 and 20 interactions in which the student must enter an answer, click an object, or make a decision of some kind. The general approach is similar to what a good teacher would do in a one-on-one session: ask questions whose answers lead to further questions, forcing the student to actively engage with the material and to build upon existing knowledge. Extensive documentation is available for reference and review.

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