COMPOSITION, REACTION, AND EQUILIBRIUM

Experiments in Chemistry

Craig, Carlton, Ackermann, Schoonmaker, and Renfrow

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Composition, Reaction, and Equilibrium

Experiments in Chemistry

Reading, Massachusetts · Menlo Park, California · London · Don Mills, Ontario

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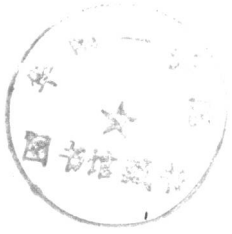
Francis T. Bonner
Consulting Editor

THE PERIODIC TABLE, SHOWING THE SEPARATION INTO THE *s*-, *p*-, *d*-, and *f*-BLOCKS

																	2 He 4.003
1*s*	1 H 1.0080											2*p*	5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.9994	9 F 19.00	10 Ne 20.183
2*s*	3 Li 6.939	4 Be 9.012										3*p*	13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
3*s*	11 Na 22.9898	12 Mg 24.312										4*p*	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.909	36 Kr 83.80
4*s*	19 K 39.102	20 Ca 40.08	3*d*	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37				
5*s*	37 Rb 85.47	38 Sr 87.62	4*d*	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc [99]	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	5*p*	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
6*s*	55 Cs 132.91	56 Ba 137.34	5*d*	57– La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.23	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	6*p*	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po [210]	85 At [210]	86 Rn [222]
7*s*	87 Fr [223]	88 Ra [226]	6*d*	89– Ac [227]	104									7*p*						

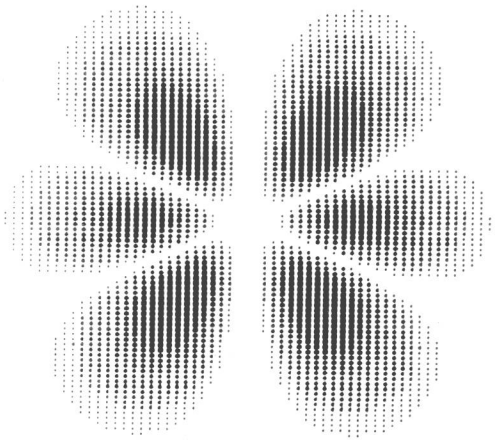
4*f*	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [147]	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
5*f*	90 Th 232.04	91 Pa [231]	92 U 238.03	93 Np [237]	94 Pu [242]	95 Am [243]	96 Cm [247]	97 Bk [249]	98 Cf [251]	99 Es [254]	100 Fm [253]	101 Md [256]	102 No [253]	103 Lw [257]

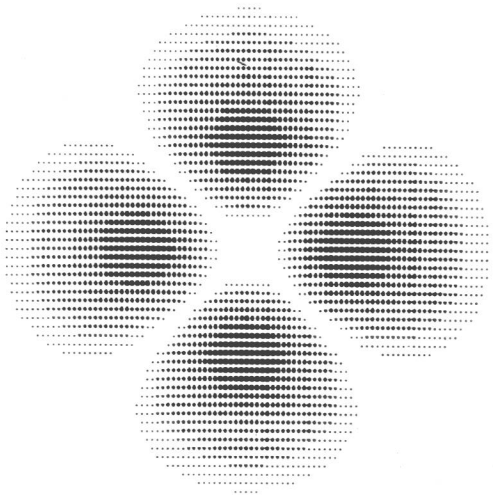
To a generation of Oberlin students

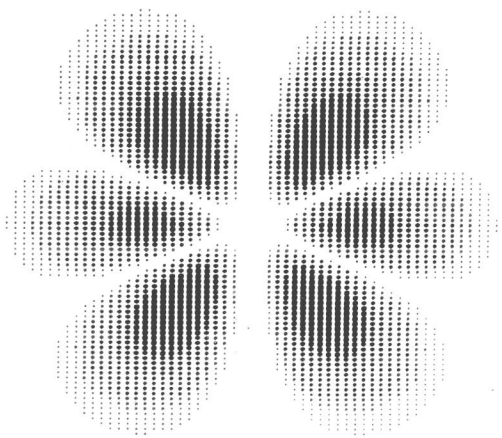


Pictured on this page are three cross-sections of the electron probability density (ψ^2) for a $5g_2$ hydrogen-like atomic orbital. For the figures from lower left to upper right, the vertical and horizontal axes are respectively: z,x; x,y; and z,y. From the number and disposition of nodal features, one can identify an orbital. The total number of nodal surfaces (planes, cones, and spheres) is n-1, where n is the principal quantum number. The number of vertical nodal planes is m, the magnetic quantum number. The number of nodal planes and cones is l, the angular momentum quantum number. The number of spherical nodal surfaces is n-1-l.

The figures were produced by a computer from a program written by David D. Sherertz.







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Preface

In this laboratory manual we have attempted to assemble a group of experiments which can serve a wide range of general chemistry programs. There are more experiments than can be completed in the typical two-term laboratory program. The experiments differ considerably in the level of mathematical analysis required and in the use of instrumentation. The qualitative analysis section can be omitted or readily adapted to many or few laboratory sessions. In almost every case the experiments are self-contained and therefore can be arranged in an order suited to a particular course. We hope that the manual invites supplementation with experiments of local issue.

The manual has been developed for a course which enrolls a range of students extending from those who study chemistry as part of a college distribution requirement to those who may decide to major in chemistry. We do not assume a calculus prerequisite or corequisite for the course. We do assume a willingness on the part of the students to increase their skill in applying quantitative arguments. A few of the experiments originated in our honors level course, and many are suitable for use in such a program.

Several experiments are intended for use in a course which includes a substantial introduction to chemical thermodynamics. In this regard the notes on qualitative analysis ("Inorganic Qualitative Analysis. Part A. Theory") deserve special mention. These notes make much use of thermodynamic arguments as well as the theory of solution equilibria and other principles. The qualitative analysis is thus a vehicle for developing skill in applying a variety of chemical principles in concert. In the qualitative analysis material and in other experiments we have emphasized use of the categories *acid-base, oxidation-reduction, precipitation*, and *complex-forming* to help organize inorganic reaction chemistry.

We believe that chemical synthesis should be a significant part of the general chemistry laboratory program. There are several synthesis experiments, and in each case the student can go on to use or investigate the material he has synthesized. Thus, the coordination compound of copper is analyzed for copper ion, ammonia, and sulfate ion contents, and its thermal decomposition is studied. The *p*-xylenesulfonic acid is useful as a standard in subsequent acid-base titrations. The ethylenediamine complex of the cobalt-

(III) ion is used in a rate study. Of course, if one does not elect to include these syntheses in a laboratory program, another acid standard can be substituted in the titration experiment, and the cobalt compound can be supplied for the rate study.

The design of the experiments reflects the practices in our laboratories, but the experiments can be readily adapted to other programs. The theory section of each experiment is sufficiently complete that laboratory lectures are unnecessary. This feature makes it possible for several experiments to be active at a given laboratory session—a practical necessity when a number of experiments require access to limited equipment. In organizing a term's work we have found *cycles* to be a useful device. Each cycle consists of four or five experiments only some of which involve instruments, and a term may consist of three cycles. One cycle may be devoted to qualitative analysis with the experiment on infrared analysis serving as a capstone. A student works within a cycle of experiments in an order governed by his interest and the availability of instruments. A cycle may also include choices between experiments involving similar techniques, such as the two experiments on the enthalpy of reaction or the two on the half-life of radioisotopes. We believe that the laboratory is a livelier place under the cycle plan. There is a variety of activity in a laboratory session, and students make helpful suggestions to one another based on prior experience with an experiment. When a student has completed a quantitative experiment he reports his results to a member of the staff. At the end of each cycle the student turns in for examination by the staff the bound notebook in which he has recorded observations and data, performed calculations, and answered questions.

Many of the experiments are "open-ended." In some cases, such as the experiments on crystal structure and on the equilibrium constant for the thiocyanatoiron (III) complex, we have provided explicit instructions for extending the studies. In other cases, such as the synthesis and analysis of a coordination compound of copper, alternative procedures and further studies are merely outlined, with helpful references cited. Still other experiments, such as qualitative analysis and the one on classifying species

according to reactivities, provide the student with a theoretical background and a *modus operandi* but then place him on his own to devise specific experiments. Most of the other experiments which are not explicitly open-ended are such that the instructor or the student will recognize openings for further studies.

In the manual we have not included instructions for use of the analytical balance. To cover the range of analytical balances likely to be found in general chemistry laboratories it would be necessary to describe a number of types in some detail. Furthermore, where single-pan automatic balances are used, instructors differ in the extent to which they choose to present the theory of the analytical balance to general chemistry students. In the manual the section on general instructions in other laboratory techniques has been kept to a minimum. Discussions of techniques such as filtration and titration and instructions for the use of instruments such as the spectrophotometer or pH meter are presented in connection with individual experiments.

Although the digital computer is not essential to the laboratory program, we have encouraged students to make use of it. The experiment on the Balmer spectrum of atomic hydrogen includes a program, written in FORTRAN IV, to assist in the data reduction. With this supplement the experiment enjoys a better reputation among students than it did when computations had to be done by hand. Students are also encouraged to write their own programs or to adapt existing programs for use in the experiments on the thiocyanatoiron (III) complex and on reaction rates.

Some of the experiments in the manual are novel. Some are adaptations of well-known experiments. Those of recent and identifiable parentage are referenced as to source. We wish also to take this opportunity to acknowledge the many contributions of Luke E. Steiner, J. Arthur Campbell, and Carl W. Kammeyer to the general chemistry laboratory program at Oberlin College.

Oberlin, Ohio
May 1970

The authors

LIST OF THE ATOMIC WEIGHTS OF THE ELEMENTS

Element	Symbol	Atomic Number	Atomic Weight
Actinium	Ac	89	227
Aluminum	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.948
Arsenic	As	33	74.92
Astatine	At	85	(210)
Barium	Ba	56	137.34
Berkelium	Bk	97	(249)
Beryllium	Be	4	9.012
Bismuth	Bi	83	208.98
Boron	B	5	10.81
Bromine	Br	35	79.909
Cadmium	Cd	48	112.40
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.011
Cerium	Ce	58	140.12
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.453
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	(247)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(254)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(253)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Helium	He	2	4.003
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0080
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lw	103	(257)
Lead	Pb	82	207.19
Lithium	Li	3	6.939
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.94
Mendelevium	Md	101	(256)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.183
Neptunium	Np	93	(237)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.007
Nobelium	No	102	(253)
Osmium	Os	76	190.2
Oxygen	O	8	15.9994
Palladium	Pd	46	106.4
Phosphorus	P	15	30.974
Platinum	Pt	78	195.09
Plutonium	Pu	94	(242)
Polonium	Po	84	(210)
Potassium	K	19	39.102
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(147)
Protactinium	Pa	91	(231)
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.23
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85,47
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.870
Sodium	Na	11	22.9898
Strontium	Sr	38	87.62
Sulfur	S	16	32.064
Tantalum	Ta	73	180.95
Technetium	Tc	43	(99)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

* Based on mass of C^{12} at 12.000 . . . The ratio of these weights to those on the older chemical scale (in which oxygen of natural isotopic composition was assigned a mass of 16.0000 . . .) is 1.000050. (Values in parentheses represent the most stable known isotopes.)

Contents

General Instructions

The following advice and instructions are applicable to laboratory work in general. You should observe these points at all times.

SAFETY

Accidents in a well-run laboratory are rare and very seldom of a serious nature. However, the potential for injury is always present, and safety precautions must be rigorously observed. Promptly notify an instructor if you or a neighbor has an accident. The instructor will know about first aid and medical facilities.

You should wear glasses in the laboratory at all times. Your own glasses are acceptable. Otherwise, make arrangements for acquiring a pair of safety glasses during the first laboratory period. If any liquid splashes into your eye, *immediately* wash the area copiously under running water, keeping the eye open as much of the time as possible. Note the location of eyewash fountains or water faucets that might be used.

Many of the chemicals which you will use are poisons, even though they are seldom labeled as such. Never take chemicals into your mouth, and keep your hands out of your mouth until you have washed them. It is advisable to wash your hands just before leaving the laboratory. Never bring food or beverages into the laboratory. Hydrogen sulfide, nitrogen dioxide, and some of the other gases you will use are poisons. Make and use them (or any unpleasant gas) only on the specially ventilated benches (called hoods).

Do not leave a burner lighted when it is not in use. Never put into your drawer a piece of apparatus which is too hot to handle. When working with acetone, ether, and other flammable, volatile liquids, keep them in covered containers when possible and away from flames.

Note the location and method for operation of fire extinguishers and safety showers.

A number of chemicals can damage skin and clothing. Concentrated nitric and sulfuric acids and sodium hydroxide are the most commonly used chemicals of this type. Hydrofluoric acid and bromine cause particularly bad chemical burns. Wash the skin (or clothing) immediately with plenty of water if you are splashed with a corrosive chemical.

When diluting acids, add the acid to the water. The reverse process may generate enough heat at the interface of the water and the denser acid to break the container or cause spattering. Stirring and slow addition of acid to water help to distribute this heat.

A liquid which is being heated in a test tube is liable to be ejected a considerable distance due to the sudden formation of vapor bubbles. Never point the mouth of a test tube at yourself or another person while it is being heated. The following precautions will help to prevent ejection of hot liquid.

1 Do not attempt to boil liquid in a test tube that is more than a quarter filled.

2 Hold the test tube at about a 45° angle with the vertical.

3 Heat the tube near the liquid surface, not at the bottom.

4 Use a small flame.

5 Stir continuously with a stirring rod.

6 If only heating, not active boiling, is required, put the test tube in a beaker of boiling water instead of heating it directly over a flame. Boiling is useful only to drive off dissolved gases or to rapidly evaporate part of the solvent.

Do not inhale vapors unless there is a good reason for doing so. Hold the vessel several inches from your nose, and fan the vapor toward your nostrils. Take several small sniffs, not one big draught.

Do not use cracked or broken glassware or porcelain. You will have to replace it at checkout time anyway, so replace it immediately upon breaking and before it causes an accident.

Everyone is expected to do his part in keeping the laboratory clean, orderly, and safe. Promptly clean up any spills. Flush liquid wastes down the sink with plenty of water. Dispose of solid wastes in the containers provided. Return bottles of chemicals to their proper locations.

REAGENTS

Pure chemicals for laboratory use are known as reagents. Most of the reagents that you will use are available in the laboratory. Never take a reagent bottle to your desk. Someone else may need it the moment you leave. Instead, take clean test tubes or other containers with you when you go to the reagent shelves. If a ground-glass stopper is stuck in a bottle of liquid, tilt the bottle to let the liquid seep into the ground region. Hold the stopper in place, for the resulting lubrication may let the stopper fall out. If this procedure does not free the stopper, ask the instructor for help. Turn in empty reagent bottles for refilling.

Since the same reagents are used by many people, it is most important that these chemicals remain uncontaminated. Never insert a spatula, medicine dropper, or other utensil into a reagent bottle, even if you think that the utensil is clean. You should discard any unused portion of a reagent; do not return it to the bottle. Therefore it is important that you take only what you need. As a further precaution against

FIG. 1 Grasping a reagent bottle and stopper for pouring.

contamination, do not touch the bottom of a reagent bottle stopper or let this part of the stopper touch the bench top. Remove the stopper by grasping it between your index and middle fingers with the palm up. This method of holding the stopper leaves the thumb and the other fingers free for holding the bottle while the other hand is free for holding the vessel that will receive the liquid, as shown in Fig. 1.

LABORATORY NOTEBOOK

Your notebook should contain all your raw experimental data, clearly identified, and intelligible notes on your observations. Do not use loose pieces of paper for temporary recording of data. The notebook should also contain sample calculations, clearly set up in algebraic form and labeled with units throughout. Space need not be wasted on details of arithmetic, as slide-rule accuracy is regarded as adequate for most multiplication and division in this laboratory. Answer in your notebook the questions which appear at the end of each experiment. Date the pages in the notebook, and supply them with running titles, usually the titles of the experiments. Maintain an up-to-date table of contents at the rear of the notebook. Your instructor may give you other instructions regarding the notebook and the recording and reporting of results.

For increased clarity, strike through any incorrect notebook entries with a single line rather than erasing, obliterating or modifying them. Then write the corrected informa-

tion, with an arrow if necessary to show where it belongs. The notebook is a working document and is not expected to be a masterpiece of calligraphy. Nevertheless it should be legible and clear to one who reads it without having you present to explain what you meant.

MISCELLANEOUS TECHNIQUES

BUNSEN BURNER

The sequence of steps in lighting a Bunsen burner is the following. See Fig. 2.

1 Attach the burner to a gas outlet by means of rubber tubing.

2 Close the air ports by screwing the vertical tube downward.

3 Close the gas needle valve at the base of the burner by screwing it upward. To avoid damaging the valve, close it gently.

4 Open the gas outlet fully by turning the handle until it points in the direction of the nozzle.

5 Light a match and hold it at the top of the burner. Holding the match slightly to one side of the opening will keep the initial rush of gas from extinguishing the match.

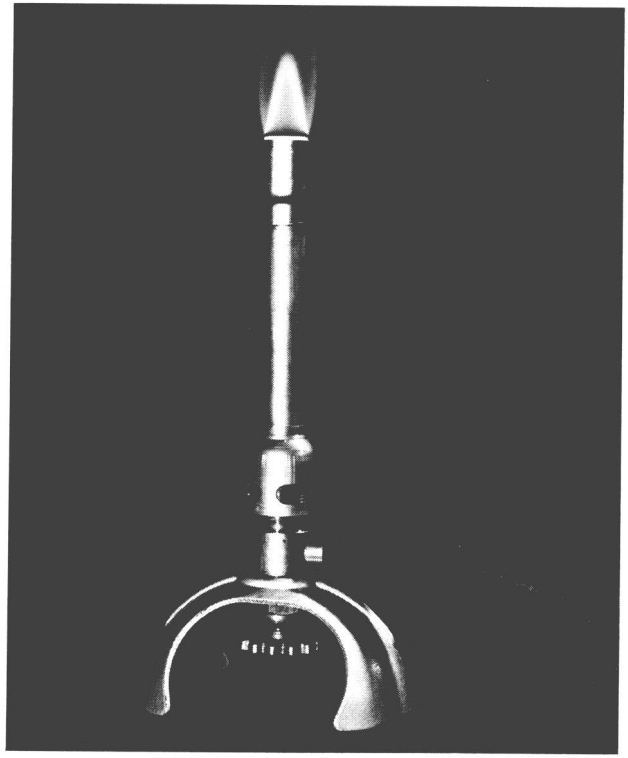

FIG. 2 Bunsen burner adjusted to give a hot flame.

6 Slowly open the needle valve until the burner ignites.

7 Adjust the needle valve and the air ports (by turning the vertical tube) to produce a flame of suitable size and temperature for the purpose at hand. When the air ports are opened, air is drawn in through them by the upward rush of gas in the vertical tube and the flame becomes hotter. The hottest flame has a light-blue inner cone and a faintly colored outer flame.

GLASS TUBING

The first step in breaking glass tubing is to lay the tubing on the desk and firmly make a single scratch with your file. Apply a drop of water to the scratch, and hold the tubing horizontally in front of you with the scratch pointed away. Push forward with your thumbs meeting directly behind the scratch while pulling backward with your fingers; the tube should snap in two. You can protect yourself from cuts by covering the tubing with a towel before breaking it. The tubing should break easily—do not force it.

The ends of any piece of glass tubing should be completely smooth before the glass is inserted into a stopper or rubber tubing. Fire-polish a sharp edge by rotating it in a hot flame until it is smooth.

Attempts to insert a glass tube or a thermometer through a rubber stopper can result in serious cuts unless the following precautions are observed. The tube end must be smooth and should be lubricated with glycerol (also called glycerin). Grasp the tube *within one inch* of the end which will go into the stopper. A slight twisting *(not bending)* motion as you insert the tube may facilitate its passage through the stopper. *It is very important* that you *never* grasp the tube more than one inch from the stopper while inserting it. Otherwise you may snap the glass in two and run a jagged edge into your hand. Since glycerol is water soluble, it can be rinsed off after the tube has been inserted the desired distance through the stopper.

WEIGHING

Triple-beam or trip balances are available for rapid weighings to an accuracy of 0.1 g (or possibly 0.01 g). When you want to weigh a sample of solid, place a container, such as a square of glossy paper (available near the balance), on the balance pan. Adjust the sliding weights until the balance pointer moves as far to one side of the zero mark as to the other when the balance is swinging. Record the weight. Place the solid to be weighed in the container, and adjust the weights until equal swings are again attained. Subtract the weight of the container from the weight of the solid plus the container.

The more delicate analytical balances are used for weighings to an accuracy of 0.1 mg (0.0001 g). You will be given separate instructions for these balances. Either kind of balance is likely to become corroded unless you clean up spills promptly.

READING LIQUID LEVELS

The surface of a liquid in a narrow tube is not flat, but curved, and the curved surface is called a meniscus. The meniscus of water, and other liquids which wet glass, is concave