Basic Chemistry for Electroplaters

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An understanding and recognition of chemical reactions is necessary for an appreciation of the changes that occur at metal surfaces during plating and surface finishing operations. The rules involving chemical calculations will enable one to make appropriate additions of chemicals to properly control the various baths. This article is offered with these aims in mind.

All materials on earth, and indeed the universe, are believed to be comprised of some 90 *naturally* occurring substances that are called elements. A list of the elements is shown in Table 1. The elements cannot be broken down into simpler substances by chemical means. All other substances come about by chemical combination of two or more of the elements.

It may seem remarkable that the tremendous variety of animal, vegetable or mineral objects are made up of only 90 elements. In fact, only about 30 or 40 of these elements make up the vast majority of known substances. It may make it easier to understand this concept by recognizing that all the words of the English language are comprised of combinations of only 26 letters.

A shorthand method used by chemists to identify the elements is by assignment of a one- or two-letter symbol, as shown in Table 1. These symbols enable chemical reactions to be readily transmitted and understood.

Atoms

An atom can be thought of as being subdivided into smaller and smaller particles, until the smallest part or building block is reached that retains all characteristics of the element. This building block is called the **atom** (derived from the Greek word for indivisible). A visible speck of an element contains many billions of atoms, so you can appreciate how very small the atoms are. All atoms of a given element are alike for all practical purposes.

Compounds

When elements combine, they form what are called compounds. The compounds are often completely different in properties than the elements, which helps explain the amazing diversity found in nature. Sodium (a metal that burns or explodes in the presence of water), for example, reacts with chlorine (a poisonous yellowish gas) to form the compound sodium chloride (ordinary table salt).

Molecules

The atoms of the various elements react to form compounds. The smallest part of a compound is called a molecule, which will always contain a whole number of atoms. In some instances, two identical atoms—particularly of certain gaseous elements—will combine to form molecules. Examples are hydrogen (H_2), oxygen (O_2), chlorine (Cl_2) and nitrogen (N_2). Subscripts are used to identify the number of atoms (if more than one) in a molecule.

To express the reaction between sodium and chlorine described above, we could say that: One atom of Na + one atom of Cl → one molecule of NaCl, or simply:

$$Na + Cl \rightarrow NaCl$$

Chlorine, however, exists as the diatomic molecule Cl_2 so the chemical reaction which represents reality would be:

$$2Na + Cl_2 \rightarrow 2NaCl$$

The number of atoms in the reactants must be the same number as in the product(s). Appropriate numbers give the number of atoms or molecules involved and are said to balance the equation. When no numeral precedes the atom or molecule, the number 1 is assumed.

Atomic Weight

An atom can simplistically be pictured as having a nucleus containing the subatomic particles, protons (positively-charged) and neutrons (neutral charge). Electrons (negatively-charged particles of electricity) spin around the nucleus in a number equal to that of the protons in the nucleus. The protons and neutrons are roughly equal in weight and make up essentially the entire weight of the atom, because the weight of electrons is relatively negligible. Thus, if we assign an arbitrary weight unit of "one" to the proton or neutron, the total number of protons and neutrons in an atom represents the atomic weight of that atom/element. Table 2 shows the 12 elements of lowest atomic weight, along with the heaviest of the naturally-occurring elements.

The numbers in columns 2, 3 and 5 are identical, because the atomic number is defined by the number of protons in the nucleus and the number of electrons must be identical to the number of protons to achieve the mandatory electrical neutrality of the atom.

You may note that atomic weights of some elements are not even close to whole numbers. This is because a significant portion of the atoms may contain a different number of neutrons and the atomic weight represents an average. For example, there are about three times as many chlorine atoms with 18 neutrons (Cl-35) as there are with 20 neutrons (Cl-37), so that the atomic weight will be roughly 35.5. Atoms of an element with different numbers of neu-

Table I
Table of the Elements

	Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97
Antimony	Sb	51	121.76
Argon	Ar	18	39.944
Arsenic	As	33	74.91
Barium	Ba	56	137.36
Beryllium	Be	4	9.02
Bismuth	Bi	83	209
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Carbon	C	6	12.01
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Copper	Cu	29	63.57
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152
Fluorine	F	9	19
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.6
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.008
Indium	In	49	114.76
Iridium	Ir	77	193.1
Iodine	I	53	126.92
Iron	Fe	26	55.85
Krypton	Kr	36	83.7
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.94
Lutecium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95

	Symbol	Atomic Number	Atomic Weight
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Niobium (Columbium)	Nb (Cb)	41	92.91
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16
Palladium	Pd	46	106.7
Phosphorus	P	15	30.98
Platinum	Pt	78	195.23
Potassium	K	19	39.096
Praseodymium	Pr	59	140.92
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	86.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.1
Selenium	Se	34	78.96
Silicon	Si	14	28.06
Silver	Ag	47	107.88
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.066
Tantalum	Ta	73	180.88
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.7
Titanium	Ti	22	47.9
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

trons are called isotopes of the element. Yet, they have the same chemical properties.

Valence

Molecules are formed by combinations of whole numbers of atoms only; the number of various atoms that can combine is governed by what is called the valence. The valence is often based upon the number of electrons in the outermost shell of the atom, though we will not delve into this matter here. Table 3 shows examples of some elements and their usual valence. The elements of (+) valence combine with those of (–) valence so that the resulting compound is electrically neutral. Some elements can have more than one valence, examples of which are shown in Table 3. When groups of atoms behave as a unit in chemical reactions, these groupings are called radicals.

When more than one unit of a radical is needed to produce an electrically neutral compound, the radical is enclosed in parentheses and the number of radicals in the compound is denoted by the appropriate subscript numeral. For example, ammonium sulfate would be $(NH_4)_2SO_4$ and zinc cyanide would be $Zn(CN)_2$.

Elements of positive (+) valence are generally metals, while those of negative (–) valence are nonmetals. The valences must be memorized or can be determined from knowledge of compound make-up. For example, if you know the compounds HCl, H_2O and $NiCl_2$ exist, then you can infer that nickel oxide would have the molecule NiO.

When an element has more than one valence, the lower valence is called the "-ous" form and the higher, the "-ic" form. So SnO_2 would be called stannic oxide and SnO would be stannous oxide. $FeCl_2$ is called ferrous chloride and $FeCl_3$ is ferric chloride.

Nomenclature

When hydrogen is combined with elements or radicals of negative valence, the compounds are called acids and end in "-ic." (HCl is hydrochloric acid, H_2SO_4 sulfuric acid, H_3PO_4 phosphoric acid.)

When other elements or radicals of positive (+) valence combine, the products are called salts and the name ends in "-ide" or "-ate". (NaCl is sodium chloride, $NaNO_3$ is sodium nitrate and NaCN is sodium cyanide.) In general, when a negative valence radical contains more than one oxygen atom, the salt name ends in "-ate"; otherwise the salt name ends in "-ide." There are, however, exceptions to this rule.

Compounds that contain the OH radical are called hydroxides. (NaOH is sodium hydroxide, $Ca(OH)_2$ is calcium hydroxide and $Fe(OH)_3$ is ferric hydroxide.)

Ions

Many compounds that are dissolved in water can dissociate (ionize) to form positively (+) or negatively (–) charged particles (ions) in accordance with the valence of the constituent elements or radicals. For example, the salt $ZnSO_4$ will ionize to form Zn^{+2} and SO_4^{-2} ions; $AgNO_3$ to Ag^{+1} and $(NO_3)^{-1}$; $NiCl_2$ to Ni^{+2} and 2 Cl^{-1} and H_2SO_4 to 2 H^+ and $(SO_4)^{-2}$. The presence of ions accounts for the conductivity of solutions and the ability of electrodeposition to take place. Not all substances that dissolve in water will produce ions. For example, sugar is readily soluble but does not ionize, nor does it carry electric current. Pure water is only slightly ionized and will conduct little current unless ionizable substances are present.

Chemical Calculations

Knowledge of the relative atomic weights of each element makes it possible to make calculations regarding the weights of the reactants and products of chemical reactions. For example:

$$\begin{array}{lll} C + O_2 & \rightarrow & CO_2 \\ 12 \quad 16+16 = 32 & & 12+16+16 = 44 \end{array}$$

We can write the atomic/molecular weights under the reactants and product. Thus, 12 grams of carbon will burn in 32 grams of oxygen to form 44 grams of carbon dioxide. The same relationship holds with any consistent weight units, whether pounds, tons or micrograms. It should be evident that 6 lb of carbon would require 16 lb of oxygen to produce 22 lb of carbon dioxide. A simple way of solving such problems when the answers are not evident is to set up the problem as follows:

$$\begin{array}{lll} 0.37 & & \chi \\ C + & O_2 & \rightarrow CO_2 \\ 12 & 32 & 44 \end{array}$$

Example 1

Let us say we wish to know how much CO_2 would be formed when 0.37 lb of carbon is burned in conformance with the above. We simply write X above CO_2 and 0.37 lb above carbon. The following relationship will hold:

$$\frac{\chi}{44} = \frac{0.37}{12} \;;\; \chi = \frac{0.37}{44 \text{ x } 12} = 1.4 \text{ lb.}$$

Another way of looking at this is to recognize that the ratio of CO_2 to C is $^{44}/_{12}$ and that $^{\chi}/_{0.37}$ is in the same proportion so:

$$\frac{\chi}{37} = \frac{44}{12} \;;\; \chi = \frac{0.37 \text{ x } 44}{12}$$

Example 2

Analysis of a cyanide-zinc bath indicates that it is necessary to add 20 lb of zinc. How much $Zn(CN)_2$ salt should be added?

$$\begin{array}{llll} 20 \text{ lb} & & & \chi \\ Zn & + (2CN) & = & Zn(2CN) \\ 65.4 & & & 65.4 + 2(26) = 117.4 \end{array}$$

$$\frac{\chi}{117.4} = \frac{20}{65.4} \qquad \chi = \frac{117.4 \text{ x } 20}{65.4} = 35.9 \text{ lb}$$

In other words, 117.4 lb of $Zn(CN)_2$ contains 65.4 lb of Zn and 35.9 lb of $Zn(CN)_2$ contains 20 lb of Zn. Though the above is not a true chemical reaction, the weight relationships do hold.

Example 3

What is the percent of nickel in the compound nickel sulfate hexahydrate ($NiSO_4$•$6H_2O$), which means that each molecule of $NiSO_4$ is associated with 6 molecules of water. We can write

$$\begin{array}{ll} \chi \text{ grams} & 100 \text{ grams} \\ Ni + SO_4 + 6\,H_2O = & NiSO_4 \cdot 6\,H_2O \\ 58.7 & (58.7 + 32.1 + 4x16 + 6x18) = 262.8 \end{array}$$

The atomic weight of Ni is 58.7, while the molecular weight of $NiSO_4$•$6H_2O$ is 58.7 + 32.1 + 4x16 + 6x18 = 262.8. The percent of Ni is the number of grams of Ni in 100 grams of the compound. We can then use the relationship:

$$\frac{\chi}{58.7} = \frac{100}{262.8} \qquad \chi = 58.7 \text{ x } = \frac{100}{262.8} = 22.3\%$$

or simply recognize that there are 58.7 grams of Ni in 262.8 grams of $NiSO_4$•$6H_2O$ and the % nickel = $^{58.7}/_{262.8}$ x 100 = 22.3%.

Neutralization

Neutralization can be simply stated as the reaction of an acid with an alkali to produce a salt plus water. For example:

	1 g		17 g				18 g
	H Cl		Na OH		NaCl		H_2O
	acid	+	alkali	--------->	salt	+	water
mol. wt.	36.5 g		40 g		58.5 g		18 g

Common to neutralization is the fact that 1 gram of hydrogen of the acid molecule reacts with 17 grams of hydroxyl (OH) of the alkali to form 18 grams of water. This will occur when the molecular weight in grams of HCl reacts with the molecular weight in grams of NaOH. If a gram molecular weight of the acid or the alkali is dissolved to produce one liter of solution, it should be evident that any volume of the acid solution will be neutralized by an equal volume of the alkali. The solutions are called one normal (1N) solutions. The acid contains 1 g/L H and the alkaline solution contains 17 g/L OH.

By definition, a one Normal solution =

$$\frac{\text{gram molecular wt/L acid or alkali}}{\text{No. of (H) or (OH) in molecule.}}$$

The g/L of acid/alkali needed to make a 1N solution is called the gram equivalent weight. Solutions may be made up of any fraction or multiple of a one normal (1N) solution. For example, 20 g/L NaOH would be a 0.5 N solution and 73 g/L HCl would be a 2 N solution. Neutralization reactions of acids and alkalis of different normalities follow the relationship:

mL of acid x N acid = mL of alkali x N alkali.

Example 4

If we have a standard alkaline solution of 0.125 N and wish to ascertain the normality of an acid solution, we can neutralize (titrate) a known volume, for example, 25 mL, of the acid with the alkaline solution added incrementally until neutralization is achieved. Neutralization is usually indicated by an appropriate color change endpoint, or by pH measurements (measure of acidity/alkalinity). In this case, let us say that 18 mL of the alkaline solution was needed to just neutralize the acid, then:

$$25 \text{ mL x } N_{acid} = 18 \text{ mL x } 0.125 \text{ N}$$

$$N_{acid} = \frac{18 \text{ x } 0.125}{25} = 0.09 \text{ N.}$$

If the acid is HCl, then a 0.09 N solution contains

$$0.09 \text{ N x } 36.5 \quad \frac{\text{g/L of HC1}}{\text{N solution}} = 3.29 \text{ g/L HCl}$$

The following general relationship holds:

g/L in solution = Normality x g/L acid or alkali required to make a 1N solution

If the acid in the example above was H_2SO_4, then a 1N solution would contain:

$$\frac{\text{gram molecular wt } H_2SO_4}{2} = \frac{98}{2} = 49 \text{ g/L = gram equivalent wt}$$

and a 0.09 N H_2SO_4 solution would contain:

$$49 \text{ x } 0.09 = 4.4 \text{ g/L } H_2SO_4$$

The equivalent weights of some acids and alkalis are shown in Table 4.

Table 2
Subatomic Particles in Elements Of Increasing Atomic Weight

Atomic Symbol	Atomic Number	No. of Protons	No. of Neutrons	No. of Electrons	Approximate Atomic Weight
H	1	1	0	1	1
He	2	2	2	2	4
Li	3	3	4	3	7
Be	4	4	5	4	9
B	5	5	5	5	10
C	6	6	6	6	12
N	7	7	7	7	14
O	8	8	8	8	16
F	9	9	10	9	19
Ne	10	10	10	10	20
Na	11	11	12	11	23
Mg	12	12	12	12	24
:	:	:	:	:	:
U	92	92	146	92	238

Table 3
Valence of selected elements and radicals

Element	Nomenclature	Valence	Element	Nomenclature	Valence
H	Hydrogen	+1	O	Oxide	–2
Ni	Nickel	+2	Cl	Chloride	–1
Al	Aluminum	+3	F	Fluoride	–1
Ag	Silver	+1	CN	Cyanide	–1
Zn	Zinc	+2	SO_4	Sulfate	–2
Cd	Cadmium	+2	Cr_2O_7	Dichromate	–2
Na	Sodium	+1	PO_4	Phosphate	–3
Cu	Cuprous	+1	OH	Hydroxide	–1
Cu	Cupric	+2	NO_3	Nitrate	–1
Fe	Ferrous	+2	CO_3	Carbonate	–2
Fe	Ferric	+3	S	Sulfide	–2
Sn	Stannous	+2			
Sn	Stannic	+4			
NH_4	Ammonium	+1			

Table 4
Equivalent Weights of Selected Acids & Alkalis

	Molecular Weight	Equivalent Weight
HCl	36.5	36.5
H_2SO_4	98	49
H_3PO_4	98	32.7
$HC_2H_3O_2$ (Acetic)	60	60
NaOH	40	40
KOH	56	56

pH

A convenient method for measuring the acidity/alkalinity of solutions is by use of pH. The pH is a measure of the hydrogen ion concentration, as scaled below.

0 1	2 3	4 5	6 7 8	9 10	11 12	13 14
Strongly acidic	Moderately acidic	Weakly acidic	Neutral acidic	Weakly alkaline	Moderately alkaline	Strongly alkaline

A solution of pH 0 is 1N in hydrogen ions (H^+); pH 1 is 0.1N; pH 2 is 0.01N, and so forth.

Summary

The foregoing is considered the minimum chemistry knowledge required of electroplaters who conduct laboratory analyses and make bath replenishments. For somewhat more extensive treatment of the subject, readers are referred to the AESF Illustrated Lecture on Chemistry, from which some of the above material has been garnered. *P&SF*

Editor's note: *Up until now, the articles in this series have been based on material from the "AES Update" series that ran in this journal in the late 1970s and early 1980s. This month, we are pleased and honored to publish new material contributed by Fred Pearlstein, one of the pioneers in our field, and a contributor of so many articles and papers, including several of the "AES Update" articles.*