Chapter 6. Chemical Elements

6.1. Chemical Principles

Humans have been studying chemistry for as long as they have been curious about the structure, properties and behavior of material objects. Food processing, ore refining, organic growth and decay, for example, all involve practical applications of chemical changes. The *science* (or quest for understanding and control) of chemistry has no real beginning, but underwent a profound transition in the Age of Enlightenment when the practice of systematic experimentation began. A key prerequisite to progress was the concept of *reproducibility*, which meant that results could be objectively confirmed. This, in turn, required clear, unambiguous *communication* of observations. These events marked the transition between alchemical speculation and chemical understanding.[1]

Fundamental principles are statements of basic concepts and relationships that explain phenomena in the simplest terms. They represent a generalization of knowledge and understanding and are therefore able to answer specific questions related to their subject, but the principles themselves are derived from a distillation of considerable observation and analysis. Typical of observational sciences, *essentially all the basic notions of chemistry dealing with the structure and behavior of matter began as heuristic guesses conceived through careful observation and profound insight before they became established concepts through demonstratable evidence*.[2] When hypotheses become established principles, however, explanations

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[1] *Alchemists*, who trace their dubious heritage to antiquity, supported their profession by promising wealthy patrons magical *philosopher's stones* which would convert *base* metals like lead into *noble* metals like gold, secret *elixir's* that could cure disease and prolong life, and clever *perpetual motion machines* which would produce unlimited amounts of energy at little cost.

Chemists are modern credentialed scientists supported by government and industry on the pretext of producing proprietary *catalysts* which can convert *natural resources* into marketable products, patented *magic bullets* which can target diseases and prolong life, and chemical *cold fusion* which produce unlimited amounts of energy at little cost.

[2] For those already acquainted with the principles and history of chemistry we would claim that the "theories" of chemical structure, including the notions of atoms, periodicity and chemical bonding, as well as the "laws" of chemical reactivity, including the equations of chemical combination, mass action and kinetics, were all empirical concepts before they were explained in terms of more fundamental principles.

become clearer, predictions becomes more believable, and heuristic strategies become justified algorithmic prescriptions. To apply the principles of a *mature* field (like chemistry is advertised to be) to practical problems, all one should have to do then, is to invoke the algorithm appropriate to the situation. This view is a little overoptimistic, however. In the first place, the situation may be so complex or poorly defined that it may not be obvious which algorithm or algorithms to apply. In the second place, there are many situations for which the principles are not understood and the algorithms constructed. This may be forgivable considering the breadth of the scope of the field of chemistry.

From a reductionist point of view, if all matter is made of atoms which are combinations of just a few fundamental particles (Section 4.5), then shouldn't it be possible to discover the laws of behavior of these particles and, in a constructive way, explain how all matter behaves? The answer is yes and no. In fact the laws of behavior at the atomic have been worked out. They are called "wave mechanics", and take form of *wave equations*. The theory began to be worked out by physicists in 1925, and by 1929 Paul Dirac[3] could write:

> The underlying physical laws necessary for the mathematical theory of ... the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much to complicated to be solvable.[4]

So the principles were understood, they just couldn't be implemented into convenient algorithms. The algorithms in this case are the solutions to mathematical equations, equations of a class known to be rather intractable. (Section 5.7 gives an introduction to wave mechanics.) The bottom line is that the equations for the simplest systems (the smallest atoms and molecules) *can* be solved *analytically* (with pencil and paper), those for small systems can be fairly accurately solved *numerically* (with computers),[5] but far larger systems, including many of interest to chemists. Thus, while there is optimism for progress, chemistry has not yet been totally reduced to a subfield of physics or applied mathematics. There are three consequences to this situation for our purposes. First, some heuristics developed in the past by

[3] Paul Adrien Maurice Dirac (British, 1902-1976) Nobel Prize in physics, 1933. One of the formulators of quantum mechanics (along with Heisenberg and Schrödinger). Developed relativistic wave mechanics leading to quantized spin and anti-matter having *negative* energy.

[4] *Quantum Mechanics*, P.A.M. Dirac, Oxford University Press, London, 1st. ed., 1929, Preface.

[5] For an example of a numerical technique, see Section 3.6 on Solving General Equations for One Variable.

chemists have been put on a surer theoretical foundation, and provide some powerful algorithms for chemical applications. Second, the wave mechanical results obtained so far from for simpler systems may be extrapolated to provide general heuristics for more complicated systems. Third, there are many practical aspects to chemistry which have no explanations in fundamental terms. This is part of what makes the subject of chemistry appear intuitive (at least to those without the same intuition). We will try to make these distinctions clear, so that when difficulty arises, at least the source of the difficulty can be identified.

A historical perspective will be useful to introduce a few key figures and their contributions to chemistry that will be referred to as the concepts are presented. Great ideas are not usually conceived in a vacuum[6] and many individuals wove threads into the tapestry of chemistry we have today. But some large areas of the picture have well-known signatures and are worth recognizing. Four classic scientific publications from four succeeding centuries punctuated the discovery of the chemical principles that form the foundation of chemical science today: *The Sceptical Chymist*, by Robert Boyle,[7] (London, 1661) which gave an experimental prescription for identifying elements as nonreducible matter, *Traité Elémentaire de Chimie*, by Antoinne Lavoisier,[8] (Paris, 1789) which summarized the quantitative analysis of compounds in terms of masses of solids and volumes of gases, *A New System of Chemical Philosophy*, by John Dalton,[9] (Manchester, 1808, 1810 (two parts)), which associated

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[6] Dalton's famous predecessor, Lavoisier was known for inviting fellow scientists to his villa, flattering them into telling him of their latest discoveries, and then publishing their discoveries under his own name.

[7] Robert Boyle (English, 1627-1691) discovered the first law of gases, atomist, and co-founded of the Royal Society. Provided the first practical method for determining elemental matter (as undecomposable): "I mean by Elements, ... certain Primitive and Simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those call'd prefectly mixt Bodies are immediately compounded, and into which they are ultimately resolved."

[8] Antoinne Lavoisier (French, 1743-1794) established analytical chemistry, demonstrated the importance of the role of gases in chemical reactions (particularly oxygen), first showed that water was not elemental, first stated the law of conservation of mass, wrote the first textbook on chemistry. Was on the trail of the atomic theory when he was convicted by the Revolutionary Tribunal during the French Revolution. Lagrange observed, "It took but a moment to cut off that head, though a hundred years perhaps will be required to produce another like it."

[9] John Dalton (English, 1766-1844) a modest Quaker bachelor genius who discovered the laws of gas mixtures, first explained chemical reactions in terms of atomic composition and atomic mass, invented chemical symbols and formulas, first characterized color blindness, and diligently collected totally useless weather data daily for 57 years. The site of the Manchester Literary and Philosophical Society, which housed Dalton memo-

characteristic masses with atoms and molecules, and *The Nature of the Chemical Bond*, by Linus Pauling,[10] (Ithaca, 1939) which described how atoms are bound into molecules through interactions of their electrons.

6.2. Chemical Matter

Greek philosophers classified substances into various categories, such as animal, vegetable and mineral,[11] and "fire" (heat), "air" (gas), "water" (liquid) and "earth" (solid). Hindu philosophers discussed five "elements," light, space, air, water and earth; the Chinese identified another five: fire, water, earth, metal and wood. Alchemists classified compounds into "acids" (sour), "bases" (fundamental), the combination of which yielded "salts" (flavor). Metals were divided into "noble" (non-reactive) and "base" (corruptible) categories.

Homogeneous (pure) matter was observed to be either **compound** (divisible) or **elemental** (non-divisible). Only nine true elements were known to the ancients: the non-metals sulfur and carbon, the "base" metals iron, lead, copper, tin and mercury, and the "noble" metals silver and gold. By the time John Dalton published his *New System of Chemical Philosophy* in 1810, the number of elements identified had increased to forty-five. Today, more than one hundred are known, and the search for more continues. Each element has an unique name, usually chosen by the person who first identified it, and a one- or two-letter abbreviation of the name, called the *element symbol*.[12] The names of ten of the elements known

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rabilia, took a direct hit from a German bomb on Christmas Eve, 1940, which destroyed most of his papers and apparatus.

[10] Linus Carl Pauling (American, 1901-) the most influential chemist of the Twentieth Century, inventor of valence bonding theory, hybridization and resonance, predicted the existence of rare gas compounds, discoverer of the molecular theory of disease and the α helix structure of proteins. Passport taken away under the McCarthy era for opposing the nuclear arms race. Only single recipient of two Nobel Prizes: Chemistry, 1954, Peace, 1963. Probably would have been awarded a third prize for discovering the structure of DNA, but was given misleading data.

[11] In the game of *Animal, Vegetable or Mineral*, one tries to discover an object being thought of by another through a series of up to twenty questions designed to reduce all objects into hierarchies of subcategories. This illustrates René Descartes' general method for discovering truth, referred to as the "principle of systematic doubt," first announced in 1637.

[12] Three-letter Latin abbreviations of atomic number are used temporarily for newly-discovered transuranium elements which have not been given official names, such as Uns (un-nil-sept) for element 107.

anciently are Latin, the names of the remainder are English, with the exception of tungsten, which has the German name wolfram (symbol W). The Latin names [meanings] and (symbols) corresponding to the English names are *argentum* [white] (Ag) for silver, *aurum* [shining dawn] (Au) for gold, *cuprum* [from Cyprus] (Cu) for copper, *ferrum* [iron] (Fe) for iron, *hydrargyum* [liquid silver] (Hg) for mercury, *kalium* [alkali] (K) for potassium, *natrium* [headache remedy] (Na) for sodium, *plumbum* [heavy] (Pb) for lead, *stannum* [alloy of silver and lead] (Sn) for tin, and *stibium* (Sb) for antimony. Latin is used for the elements known to antiquity, and for potassium, sodium and antimony, which are derivatives of compounds of the elements known anciently. The English names for sulphur or sulfur (S), and carbon (C) are inherited from antiquity.

6.3. Atomic Theory

The idea that matter is atomic in nature is not new. The Greek philosophers had arrived at the logical conclusion that matter must either be continuous or discrete, that is, it must either be infinitely or finitely divisible. consider these fragments from Lucretius, a First Century B.C. atomist:

> Whatever is seen to be sentient is nevertheless composed of atoms that are insentient... The number of different forms of atoms is finite... The number of atoms of any one form is infinite... Material objects are of two kinds, atoms and compounds of atoms... The atoms themselves cannot be swamped by any force, for they are preserved indefinitely by their absolute solidity.[13]

Indeed, the term *atom* comes from the Greek *a-tomos*, meaning "not cut".

Modern chemistry developed from quantitative[14] statements about matter, specifically that matter may be analyzed and characterized by quantitative measurements, and that matter is made of fundamental units called **atoms** and combinations of atoms in fixed ratios, called **molecules**. John Dalton's contribution was not so much the notion that matter is atomic or molecular in nature (which was an old idea), but rather the vision that molecules are

[13] Lucretius, *The Nature of The Universe*, Penguin Books, 1951. Sentient means capable of observing, conscious.

[14] *Quantitative* refers to measurable quantities in terms of numbers and units. *Qualitative* refers to nonquantitative features, characteristics or attributes.

collections of *finite* numbers of atoms selected from a *finite* number of types, called elements (which was a new idea). Based on this model he invented a graphical notation scheme to describe atoms, labeling them as spheres with letters symbolizing the element to which they belonged. Although confirmed by direct observation today, atoms would have to be magnified a millionfold to be barely visible to the eye. Because of this, Dalton's model might more appropriately be called the atomic *hypothesis*. At best it was a model that at the end of the Nineteenth Century was called into question because there had been no direct observation of atoms up to that time. Nevertheless, Dalton's methods formed a powerful, if not provable, *heuristic* for predicting the behavior of chemical substances.[15]

Dalton based his atomic theory of matter on the notion that matter at the smallest scale is comprised of molecules containing atoms of elements having characteristic masses. Chemical **compounds** are substances comprised of two or more elements. From the observation that *elements react to form compounds in constant mass ratios* (Law of constant composition), Dalton deduced the mass ratios of the elements, called **relative atomic masses**. Hydrogen, being the lightest known element, was arbitrarily assigned an atomic mass value of unity. The remaining elements then had atomic masses larger than 1.[16]

The values of relative atomic masses derived from experiments depend on the *number* of atoms of each element in molecules, as indicated by subscripts on element symbols in **chemical formulas**. Simple chemical formulas have the general form $\Pi\Pi E_{n_i n_j}$, a concatenation (string) of element symbols E with subscripts n_i indicating the number of atoms of element E and n_j indicating the number of polyatomic groups.[17] The double product indicates more complicated chemical formulas which may contain parenthetical, bracketed and dotted

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[15] The uncertainty of the atomic model is illustrated by the debates over the atomic masses. Diatomic elements (two atoms combined as an elemental molecule) caused particular problems. For example, there were conflicting values reported for the mass of chlorine relative to hydrogen, 35½ and 71. Dalton preferred integer atomic masses and rejected the fractional value. The debate was settled after Dalton's death in 1844 by a *vote* of the scientific community (in favor of the fractional value now known to be correct).

[16] Since early atomic mass determinations produced values close to integers, William Prout speculated in 1815 that all elements were combinations of the simplest element, hydrogen. Although not entirely true, this notion was justified by the discovery of protons and neutrons, subatomic particles of nearly equal mass, and common to the nuclei of all elements, where the majority of the mass of the atom resides.

[17] Chemists traditionally drop subscripts equal to unity.

nested groups of elements with their subscripts to suggest the bonding and geometric arrangement of the atoms. Example: $2K_4[Mn(CN)_4].3H_2O$. Chapters 9 and 10 give further discussion on chemical formulas and names. Dalton assumed that the simplest compound molecules contain only one atom of each element. Thus he wrote H for the element hydrogen, O for oxygen, and HO for the chemical formula of the compound water. From the experimental fact that oxygen combines with hydrogen in an 8 to 1 *mass* ratio, Dalton deduced the atomic mass of oxygen to be 8 relative to hydrogen being 1. But his deduced mass ratio of 8 to one was off by a factor of two because he assumed only one atom of hydrogen combined with one atom of oxygen in water, whereas we now know that two atoms of hydrogen combine with one atom of oxygen to make two molecules of water. It can be shown experimentally and theoretically[18] that hydrogen and oxygen are *diatomic* molecules (H_2 and O_2), and that the formula for water is H_2O, but without further evidence, Dalton made reasonable assumptions. Given this current knowledge, a single oxygen atom is measured to be 8 times as heavy as *two* hydrogen atoms, or 16 times heavier than *one* hydrogen atom.

The idea that all atoms of an element have a characteristic constant mass proved extremely useful in summarizing mass relationships in chemical reactions. Once a scale of atomic masses could be established,[19] *molecular masses* (relative masses of molecules) could be calculated, (given molecular formulas), and predictions could be made of the amounts of chemical substances involved in chemical reactions. These subjects, for which we lay a foundation here, are developed later in the book.

6.4. Chemical Moles

What about the *units* of atomic mass? Although *relative* masses could be measured experimentally in the Nineteenth Century, there was no way to determine *absolute* atomic masses directly since atoms are immeasurably tiny. Nevertheless the notion of an atomic structure of matter permitted the development of an **atomic mass scale**, based on the **atomic**

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[18] From mass spectroscopic measurements and by solving Schrödinger's equation, respectively, as discussed in later chapters.

[19] Conceivably by reacting all known elements with hydrogen, practically by reacting oxygen directly with hydrogen, and then reacting oxygen with other elements, theoretically by reacting elements with carbon taken as a standard.

mass unit (amu), (also called the **Dalton** in honor of John Dalton), approximately equal to the mass of a single hydrogen atom (the lightest element). The amu today is defined as precisely 1/12*th* the mass of a single ^{12}C atom (carbon-12 isotope; isotopes are discussed in Chapter 7). On this scale, hydrogen has a mass of 1.00794 amu. Relative to hydrogen being one atomic mass unit (to two significant figures), the mass of one atom of carbon is 12, the mass of one atom of nitrogen atom is 14 amu, the mass of an oxygen atom is 16 amu, and so forth. Chlorine is unusual in that it has two abundant isotopes with different masses, giving it an *average* atomic mass of 35½ (cf. Eq. (7.1)).

A convenient *macroscopic* unit of mass for elements, called the **molar mass**, is also based on the mass of carbon. The reasoning goes, if one carbon atom has 12 times the mass of one hydrogen atom, then *one dozen* atoms of carbon must have 12 times the mass of *one dozen* hydrogen atoms. Similarly the total mass of the number of atoms of carbon equal to the number of hydrogen atoms having a mass of *one gram*, must be *12 grams*. The *number* of atoms of carbon in 12 grams of ^{12}C is called the **mole**,[20] (the unit is called the mol), and *amounts of matter may be measured either in mol units (a number measure) or equivalently in mass units (a mass measure)*, provided the conversion (molar mass) is known. The numerical value of the mol is given the symbol N_A, and is called *Avogadro's number*, in honor of one of Dalton's contemporaries who speculated (correctly) that the formula for water should be H_2O, based on the hypothesis that equal volumes of gases contained equal numbers of molecules.[21] In general there are Avogadro's number of amu's in one gram of any substance.

[20] A contraction of gram *mole*cular mass. Somewhat of a misnomer because nowadays one speaks of the *gram formula mass* to more accurately represent substances which are networks containing fragments having simple molecular formulas, such as ionic solids.

[21] A speculation Dalton rejected because it suggested more complicated molecular formulas for simple substances than Dalton was willing to accept. For example, since 2 volumes of hydrogen gas react with one volume of oxygen gas to produce water, according to Avogadro hydrogen would have to be *di*atomic (H_2) if oxygen were *mon*atomic. No one at that time could understand why or how an element would bond with itself, or, if it did, why it would stop combining at only two atoms. The explanation wasn't given until the advent of quantum mechanics in the Twentieth Century (cf. Chapter 12 on chemical bonding).

$$N_A = 602,213,670,000,000,000,000,000 = 6.0221367 \times 10^{23} \quad (6.1)$$

The mass of a single atom is called the *atomic mass*, while the mass of a mol of atoms is called the *molar mass*. The *number* is the same, but the *units* are different. Oxygen has a mass of 16 *amu per atom* and also has a mass of 16 *g per mol of atoms*.

Note carefully that the mol is a *number*. It is used in chemistry for *counting* convenient-sized amounts of atoms or molecules, just as inches and eggs are counted conveniently by the dozen. Note further that, like chemical matter, some ordinary things, like oranges, are commonly measured two different (but equivalent through conversion factor) ways, by number (dozens) and by mass (pounds or kilos). It would be tempting to refer to Avogadro's number as the chemist's dozen, like the number 13 is referred to as the baker's dozen, except that, unlike the baker's dozen, the chemist's dozen is much, much larger than an ordinary dozen.

6.5. The Atomic Mol Map

The mol is a conversion factor since it converts from one set of units (individual atoms) to another (groups of individual atoms). Atomic masses with units are conversion factors too, since they are ratios that convert between mass and number (either between amus and atoms or between grams and mols). These facts may be collected into a graphic aid to solving problems involving different measures of amounts of matter, called the **Atomic Mol Map**, reminiscent of the Mass Conversion Map of Fig 2.5. It is called a *map* because it shows how various origins and destinations are connected by conversion factors. It is called *atomic* because it will be extended to molecules later.

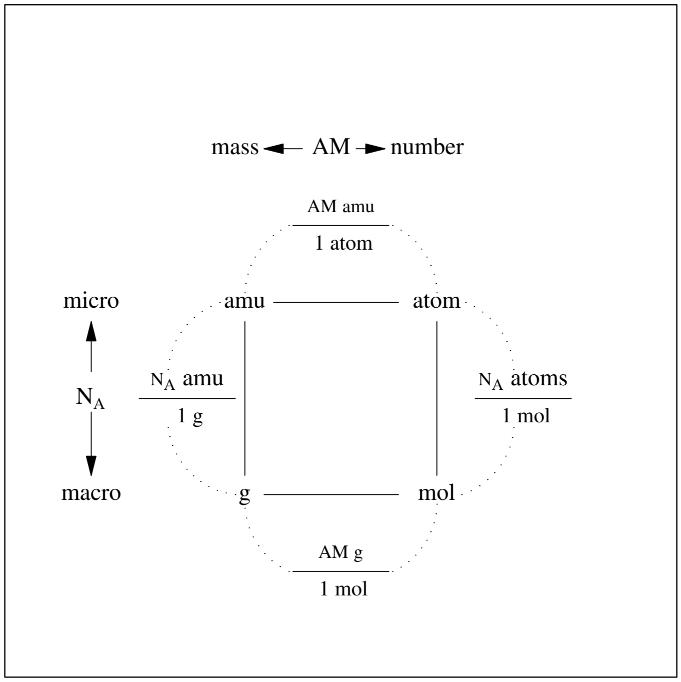

Fig. 6.1 The Atomic Mol Map

In the vertical direction, the Atomic Mol Map shows the conversion route between the *macroscopic* world of grams and mols and the *microscopic* world of atomic mass units and atoms.[22] The conversion factor which connects these two worlds is Avogadro's number, N_A, which applies equally to both sides of the Mol Map. Used in the horizontal direction, the Atomic Mol Map shows the conversion route between units of *mass* (grams and atomic mass units) and units of *number* (mols and atoms). The conversion factor which connects these two worlds is the atomic mass in the case of the microscopic quantities amu and atoms, or the

[22] *Macroscopic* objects can be seen with the unaided eye, while *microscopic* objects are too small.

molar mass in the case of the macroscopic quantities grams and mols. The same conversion factor symbol (AM) is used for both atomic mass and molar mass because the same *numerical value* applies to both (e.g. 16 for O, etc).

The Atomic Mol Map summarizes solution paths to problems involving the calculation of any of the quantities at one corner from that at any other corner. How can we derive heuristics for applications of the Atomic Mol Map? Since it employs conversion factors, the Units Conversion Heuristic of Section 2.2 comes to mind. How should that heuristic be adapted to conversions of amounts of matter? Recall that the Units Conversion Heuristic begins with the identification of the units of the given and requested quantities. This translates to identifying the origin and destination corners of the Atomic Mol Map. What remains in the Units Conversion Heuristic is the multiplication of given quantities by appropriate conversion factors to convert the units of the given quantities into those of the desired results. In applications covered by the Atomic Mol Map, these conversion factors, N_A and AM are shown explicitly along the edges of the map.

The Atomic Mol Map Heuristic

Purpose: To convert from one measure of amount of matter to another.

Procedure:

1. Identify from the statement of the problem the (given) starting and (requested) ending points on the Atomic Mol Map.
2. Determine a path on the map which leads from the starting point to the ending point.
3. Identify the conversion factors connecting the points along the path.
4. Apply the conversion factors on the edges of the Atomic Mol Map path to the given (starting point) quantity to obtain the requested (ending point) quantity.

Two examples illustrate how to use the Atomic Mol Map, one simple, the other more complicated.

Example 6.1 Consider the question, "How many amu are in one gram of iron?"

The starting place is g on the Atomic Mol Map, the destination is amu, which is adjacent to g and converted through Avogadro's number:

$$1 \text{ g Fe} \times \left(\frac{6.02214 \text{ x } 10^{23} \text{ amu}}{1 \text{ g}}\right) = 6.02214 \text{ x } 10^{23} \text{ amu Fe}$$

Note how the origin and destination are in reverse order in the statement of the problem. Also note that the unit of Fe is ignored in the conversion factor because there are Avogadro's number of amu in one gram of anything. In this way the "unit" "Fe" is carried into the answer.

Example 6.2 Now consider the question, "How many *atoms* are in one gram of iron?"

In this case the starting and ending points are not connected directly by a single conversion factor. We must choose a "flight with a layover" for the journey. The Atomic Mol Map shows two possible routes between g and atoms. (Can you locate them?) Either path should give the same final answer. We will choose the path which connects at amu. For practice, convince yourself the same result is obtained by the path connecting at mol.

$$1 \text{ g Fe} \times \left(\frac{6.02214 \text{ x } 10^{23} \text{ amu}}{1 \text{ g}}\right) \times \left(\frac{1 \text{ atom Fe}}{55.847 \text{ amu Fe}}\right) = 1.0783 \text{ x } 10^{22} \text{ atoms Fe}$$

Fe may still be left out of the conversion between g and amu, because of the generality of the conversion, but Fe can *not* be left out of the atomic mass conversion factor because the value (55.847) is specific to iron.

Summary

Substances are made of a finite number of different kinds of atoms, possibly combined into molecules. Elements are the simplest form of chemical matter. Quantitative statements can be made about atoms, even though they are invisible. Both relative and absolute masses can be determined from macroscopic measurements. Avogadro's number makes the connection between relative and absolute quantities.

The Atomic Mol Map shows how to convert between measures of amount of matter, number and mass, for both microscopic and macroscopic amounts.

CHEMICAL ELEMENTS EXERCISES

1. What is the origin of the name for Tc?
2. What is the mass in grams of 10 atoms of gold?
3. What is the mass in amu of 10 mols of gold?
4. How many different conversions does the Atomic Mol Map address?

CHEMICAL ELEMENTS EXERCISE HINTS

1. Have a look at some chemical handbook.
2. The atomic mass of gold is 196.9665.
3. The atomic mass of gold is 196.9665.
4. Don’t forget conversions can go both ways.