is found for molecules of type $[(\mu_2\text{-}BCH_3)_6(CH)_4]$ in which the boron atoms exhibit planar geometry (17).

Acknowledgment

Literature Cited

1. Flurry R. L., Jr. *J. Chem. Educ.* **1984**, *61*, 663–665.
2. Ghosh, A. *J. Chem. Educ.* **1987**, *64*, 1015–1016.
3. Hansen, P. J.; Jurs, P. C. *J. Chem. Educ.* **1988**, *65*, 661–664.
4. Perkins, R. R. *J. Chem. Educ.* **1988**, *65*, 860.
5. Davies, R. E.; Freyed, P. J. *J. Chem. Educ.* **1989**, *66*, 278–281.
6. Black, K. A. *J. Chem. Educ.* **1990**, *67*, 141–142.
7. Fort R. C., Jr. In *Adamantane—The Chemistry of Diamond Molecules*; Marcel Dekker: New York, 1976.
8. Corbridge, D. E. C. In *Phosphorus. An Outline of Its Chemistry, Biochemistry and Technology*; Elsevier: Amsterdam, 1990, Chapter 2.
9. Dance, I. G. *Polyhedron* **1986**, *5*, 1037–1104.
10. Dance, I. G.; Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. *Polyhedron* **1983**, *2*, 1031–1043.
11. Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1987**, *26*, 1683–1689.
12. Hagen, K. S.; Stephan, D. W.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 3928–3936.
13. Zhao, J.; Adcock, D.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1991**, *29*, 4358–4361.
14. Boardman, A.; Jeffs, S. E.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1984**, *83*, L39–L40.
15. Boardman, A.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1986**, *120*, L23–L24.
16. Olah, G. A. In *Cage Hydrocarbons*; Wiley: New York, 1990.
17. Rayment, I.; Shearer, H. M. M. *J. Chem. Soc. Dalton Trans.* **1977**, 136–138.

Intensive and Extensive

Underused Concepts

Sebastian G. Canagaratna
Ohio Northern University, Ada, OH 45810

Classifing the properties of material systems into extensive and intensive types embodies a very important concept. Indeed the existence of extensive properties has been raised (1) to the status of the fourth law of thermodynamics.

The use that we make of these concepts in our teaching does not do justice to their importance: Most textbooks on thermodynamics mention them only briefly, sometimes in connection with Euler's theorem. A few freshman textbooks (2–4) define them briefly, but make no use of them. The book by Bodner (5) is the only elementary text I have seen in which some use is made of these concepts.

In this article I share with the readers of *this Journal* the methods I have adopted in teaching intensive and extensive properties both at the freshman and junior levels. First I will give some background: a systematization of the facts and concepts relating to intensive and extensive properties.

Experimental Facts

Experimental facts concerning the properties of systems suggest that two important concepts are needed to describe any system: the state of the system and the size or extent of the system. This distinction implies that it is possible to prepare samples of the system that differ in extent (e.g., volume) but have the same state. The state is defined, for a pure substance, by the temperature and pressure of the sample. Thus, two samples of water both at 25 °C and 1 atm, with volumes of 25 mL and 50 mL, are said to be in the same state.

The concept of state is important because experiments suggest that certain properties—like density, refractive index, viscosity—depend only on the state and not on the size (e.g., the volume of the sample). For a homogeneous mixture, the state of the system is completely fixed by specifying, in addition to the temperature and pressure, the composition of the system (i.e., the chemical nature and relative proportion of the constituents in the mixture).

Intensive Properties

The above considerations show that there are some properties that, for a given state, do not depend on the size of the system. Such properties have, at equilibrium, the same value for all parts of a phase; indeed they have well-defined values at any point of the phase. They are called intensive properties. Their values can be used to characterize the state of the system.

Temperature and pressure are two very important intensive properties. Their intensive nature is stated in two laws: the zeroth law (law of thermal equilibrium) and the law of hydrostatic equilibrium. For a pure substance experiments show that all intensive properties depend only on the temperature and pressure. For homogeneous mixtures formed by mixing C substances, any intensive property depends, in general, not only on the temperature and pressure but also on $C - 1$ additional intensive properties, (e.g., mole fractions of $C - 1$ constituents of the mixture). Examples of other common intensive properties are density, concentration, and molality of solutes.

We can define an intensive property more formally as below.

> If α, β, γ, ... are parts of a system in equilibrium, and y is a property such that $y(\alpha) = y(\beta) = y(\gamma)$ ..., then y is said to be an intensive property.

The value of y for the system may then be defined by

$$y(\text{sys}) \equiv y(\text{any part}) \tag{1}$$

Clearly $y(\text{sys})$ is independent of the size (or extent) of the system.

Constancy of the value in all parts as given by eq 1 is the criterion for deciding whether a given property is intensive. Another way is to ask "Does it make sense to talk of the property without specifying the size of the system?" We speak, for example, of the density of water at a certain temperature and pressure, not of the density of 10 g of water or the density of 20 g of water. This shows that density is an intensive property.

Extensive Properties

In strong contrast to intensive properties are properties like volume and mass whose value for the system is the sum of values for the parts. Instead of eq 1, the properties obey the following relations.

$$V(\text{sys}) = V(\alpha) + V(\beta) + ... \tag{2}$$

$$W(\text{sys}) = W(\alpha) + W(\beta) + ... \tag{3}$$

Thus, extensive properties are additive with respective to parts of the system. For example, if a system consists of solid ice and liquid water, then

$$V(\text{system}) = V(\text{ice}) + V(\text{liquid})$$

Besides mass and volume, common examples of extensive properties include

- number of molecules
- total amount of substance, n_{tot}
- amount of component i, n_i
- mass of component i, W_i
- the thermodynamic properties
  - internal energy U
  - enthalpy H
  - entropy S
  - Gibbs free energy G

For homogeneous systems the value of an extensive property will depend on the size (or extent) of the system.

Direct Proportionality Relationships

We can make the last statement much more definite. Consider two samples of a system in the same state. Let W_1 and W_2 be the total masses of the samples 1 and 2. If

$$W_2 = r \times W_1$$

then sample 2 may be regarded as comprising r parts, each part being identical to sample 1.

If X and Y are any two extensive properties of the samples, then by the law of additivity with respect to parts of the system, we get the following.

$$X_2 = X_1 + X_1 + \ldots + X_1 \tag{4}$$

in which X_1 is added r times to give

$$X_2 = r \times X_1$$

Similarly,

$$Y_2 = r \times Y_1 \tag{5}$$

Eliminating r, we get

$$\frac{Y_2}{X_2} = \frac{Y_1}{X_1} \tag{6}$$

The validity of eq 6 is independent of r. Thus, we may summarize the significance of eq 6.

> The ratio of any two extensive properties of a homogeneous phase in equilibrium is independent of the size of the system and depends at most on the state of the system.

Thus, the ratio of extensive properties (in eq 6) is an intensive property. Equation 6 may be regarded in various ways.

- as a rationale for the definition of intensive properties
- as a basic law for extensive properties
- as giving a basis for describing the extent of a phase
- as giving a basis for checking the consistency of equations

Rationale for the Definition of Intensive Quantities

The ratio of any two extensive quantities will be independent of sample size and thus can be used to characterize the state of the system. Several common intensive properties can be correlated by eq 6.

Density

Using $Y \equiv \text{mass}$, W, and $X \equiv V$, we get

$$\left(\frac{W}{V} \right)_{\text{sample 1}} = \left(\frac{W}{V} \right)_{\text{sample 2}}$$

This gives us the following definition of density ρ for the given state.

$$\rho(\text{sample}) \equiv \left(\frac{W}{V} \right)_{\text{any sample}}$$

The density is a function of T, p, and composition.

Concentration

Using $Y \equiv$ the amount of i, n_i, and $X \equiv V$, we get

$$\left(\frac{n_i}{V} \right)_{\text{sample 1}} = \left(\frac{n_i}{V} \right)_{\text{sample 2}}$$

This gives us the following definition for the concentration of i.

$$c_i \equiv \left(\frac{n_i}{V} \right)_{\text{any sample}}$$

Thus, the concentration of i, c_i, is a function of T, p, and composition. The concentration of $C - 1$ solutes may used to specify the composition.

Mole Fraction

Using $Y \equiv n_i$ and $X \equiv$ total amount, n_{tot}, we get

$$\left(\frac{n_i}{n_{\text{tot}}} \right)_{\text{sample 1}} = \left(\frac{n_i}{n_{\text{tot}}} \right)_{\text{sample 2}} = x_i$$

where x_i is the mole fraction of i. The mole fractions are often used to specify the composition. For a given system, the mole fractions are, in contrast to concentrations, independent of T and p.

Molality

Using $Y \equiv n_i$ and $X \equiv$ mass of solvent, W_1, we get

$$\left(\frac{n_i}{W_1} \right)_{\text{sample 1}} = \left(\frac{n_i}{W_2} \right)_{\text{sample 2}} \equiv m_i$$

where m_i is the molality of i. Like mole fractions, the molalities are, for a given system, independent of T and p.

Mass Fraction

Using $Y \equiv$ mass of i, W_i, and $X \equiv$ total mass W_{tot}, we get

$$\left(\frac{W_i}{W_{\text{tot}}} \right)_{\text{sample 1}} = \left(\frac{W_i}{W_{\text{tot}}} \right)_{\text{sample 2}} \equiv \text{mass fraction of } i$$

A related intensive property is mass percentage.

Molar Mass

Using $Y \equiv W_i$ and $X \equiv n_i$, we get

$$\left(\frac{W_i}{n_i} \right)_{\text{sample 1}} = \left(\frac{W_i}{n_i} \right)_{\text{sample 2}} \equiv M_i$$

where M_i is the molar mass. Molar mass is characteristic of the substance and independent of the state.

Avogadro Constant

Using $Y \equiv$ number of molecules of i, N_i, and $X \equiv n_i$, we get

$$\left(\frac{N_i}{n_i}\right)_{\text{sample 1}} = \left(\frac{N_i}{n_i}\right)_{\text{sample 2}} \equiv N_A$$

where N_A is the Avogadro constant. The Avogadro constant is a universal constant, due to the way in which we define the amount of a substance.

Molar and Specific Properties

When Y is any extensive property of a pure substance and X is either the amount of substance n or the mass W, we obtain the following definitions of molar and specific properties, respectively.

$$\text{molar } Y \equiv \left(\frac{Y}{n}\right)_{\text{any sample}}$$

and

$$\text{specific } Y \equiv \left(\frac{Y}{W}\right)_{\text{any sample}}$$

Using the Ratio of Extensive Properties

Herron et al. (6) have recently drawn attention to the difficulties that students have with the usual definitions of density, etc. If we define density as mass divided by volume, it becomes a purely mathematical relation. Indeed the student is in danger of thinking that mass and volume are the independent variables for density! The full significance emerges only when we understand the definition in terms of eq 6.

In particular, eq 6 gives us a recipe for the experimental determination.

> Take any sample in the specified state.
> Then either select a portion of this sample of known mass and determine its volume, or select a sample of known volume and determine its mass.
> The ratio of mass to volume will give the density.

The Law for Extensive Quantities

Equation 6 is a basic law concerning extensive quantities. It can be used directly without reference to the name of any intensive quantity. I believe there is much pedagogic merit in stressing the general laws and in reinforcing them by showing how they can be used in solving problems.

Applying the Ratio of Extensive Quantities

The way I work the following problems shows how I reinforce the importance of this law.

Problem

> ➡5.0 g of oxalic acid is dissolved in 150 g of water. Calculate the mass of oxalic acid in 50 g of the solution.

Solution

The quantity that we want is W(oxalic acid), given that W(solution) = 50 g. Because these are extensive properties, the law for the problem is

$$\left(\frac{W(\text{oxalic acid})}{W(\text{solution})}\right)_{\text{sample 1}} = \left(\frac{W(\text{oxalic acid})}{W(\text{solution})}\right)_{\text{sample 2}}$$

Taking sample 1 as the solution with W(solution) = 50 g and sample 2 as the solution with W(oxalic acid) = 5.0 g and W(water) = 150 g, we have

$$\frac{W(\text{oxalic acid})}{50 \text{ g}} = \frac{5.0 \text{ g}}{5.0 \text{ g} + 150 \text{ g}}$$

Thus, we get

$$W(\text{oxalic acid}) = \frac{5.0}{155} \times 50 \text{ g}$$

### Applying Changes in Extensive Properties

Another type of question that I give students concerns the stoichiometric law for chemical reactions. These relate changes in extensive quantities and may be regarded as an example of eq 6: Changes in amounts, masses, and volumes of gases (measured at the same T and p) are proportional to one another.

One of the samples can be taken as the sample represented by the following balanced equation. Consider the following.

Problem

> • What is the mass of calcium oxide that can be prepared by the complete dissociation of 100 tons of calcium carbonate?

The equation for the reaction is

$$CaCO_3 \rightleftarrows CaO + CO_2$$
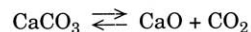
Solution

It is given that

$$W(CaCO_3) = 100 \text{ ton}$$

or more strictly, $\Delta w(CaCO_3) = 100$ ton, etc.

$$W(CaO) = ?$$

Because these are extensive quantities, we can apply eq 6, and the law for the problem becomes

$$\left(\frac{W(CaO)}{W(CaCO_3)}\right)_{\text{sample 1}} = \left(\frac{W(CaO)}{W(CaCO_3)}\right)_{\text{sample 2}}$$

Taking the balanced equation as representing sample 1, when $W(CaCO_3) = 100$ g, $W(CaO) = 28$ g. Thus, we get

$$\frac{W(CaO)}{100 \text{ ton}} = \frac{28 \text{ g}}{100 \text{ g}}$$

$$W(CaO) = \frac{28}{100} \times 100 \text{ ton}$$

There is no need to convert from ton to gram and back, as many students might do using the "dimensional analysis" approach.

Specifying the Extent of a Phase

In my treatment I stress that students should be sure their systems are completely defined before embarking on any analysis: A system is completely defined by its state and its extent. Equation 6 may also be written as

$$Y = X \times \text{intensive property}$$

To calculate an extensive property we need not only the state of the phase (to define intensive properties) but also one extensive quantity. Also, any extensive quantity is directly proportional to another extensive quantity. This makes clear the rule for describing a phase.

> A phase is completely described by specifying its state and its extent. The state of a phase is completely described by specifying its temperature, pressure, and $C - 1$ composition variables. The extent is specified by specifying any one extensive quantity.

Checks for Mistakes in Equations

Students often make careless mistakes in mathematical manipulations, so they should check for such mistakes. A check that follows from eq 6 is

If one side of an equation is extensive (or intensive), then so must be the other side.

In applying this check we must remember the following.

The product of an intensive quantity with an extensive quantity is extensive.
The ratio of two extensive quantities is intensive.
The product of intensive quantities will be intensive.

Though the quantity calculus will reveal any mistakes at the final stage, I encourage students to apply this check before starting the numerical calculation.

Laws of Conservation

There are two other ideas that I use in my systematization. The law of conservation obeyed by some extensive quantities is the following.

The value of a conserved extensive property of a closed system is independent of time and does not change even if there is a change of state.

This may be written as

The total property after the reaction =

The total property before the reaction

where the value of the total property is calculated by the principle of additivity with respect to the parts of the system.

The extensive quantities that obey the law of conservation are

- electric charge (There seem to be no exception to this.)
- the mass (This is strictly true only if we neglect small relativistic corrections.)
- the amount of each elemental species (in the absence of a nuclear reaction)
- the amount of each molecular species (in the absence of a chemical reaction)

A common mistake that students make is to assume that volume is conserved. When I ask students to predict the volume of the resulting solution obtained by mixing 200 mL of distilled water with 50 mL of 1 M NaCl solution, almost all give 250 mL as the answer. This gives me a chance to discuss the difference between additivity with respect to parts and conservation. Because there is a change of composition in the above case, volume is not conserved.

I contrast this case with mixing 200 mL of 0.1 M NaCl solution with 50 mL of 0.1 M NaCl solution, where both solutions are at the same temperature and pressure. In this example there is no change of state, and the final volume by additivity is 250 mL.

Additivity with Respect to Constituents

The last of the ideas that I use in my systematization (but only at the junior level) relates to the additivity with respect to constituents of extensive properties of a mixture. Thus, in a homogeneous mixture with the amounts n_1 for species 1, n_2 for species 2, etc., any extensive property may be written in the following form.

$$Y = n_1 y_1 + n_2 y_2 + n_3 y_3 + \dots \qquad (7)$$

where

$$y_i = \left(\frac{\partial Y}{\partial n_i} \right)_{T, p, n}$$

with y_i called the partial molar value of Y with respect to species i.

Y takes the form of a sum of contributions from each constituent, where the contribution of each constituent is for-

mally similar to that of a pure substance (i.e., $Y = ny$) except that y_i depends not only on T and p but in general also on the composition.

The following equation is an example of using eq 7 to state the Gibbs free energy.

$$G = n_i \mu_1 + n_2 \mu_2 + \dots \qquad (8)$$

Equation 8 has its basis in Euler's theorem on homogeneous functions (8). Students can write such equations more readily and work with them better when they grasp the connection between the form of the equation and the extensivity of the property.

The following equation can also be understood in terms of intensive and extensive properties.

$$dY = y_1 \, dn_1 + y_2 \, dn_2 + \dots \qquad (9)$$

It describes changes in an extensive property Y brought about by changes dn_i at constant T and p.

Equation 9 combined with eq 7 gives us the Gibbs–Duhem equations. Students find it easier, at least the first time around, to have these equations written according to their physical significance rather than by using Euler's theorem.

Introducing the Concepts: When and How?

Many of the concepts that science students encounter in high school and earlier are intensive or extensive: mass, length, volume, area, temperature, pressure, concentration. Much of the difficulty that students later experience may arise from a poor first introduction to these concepts.

An example is the way in which we introduce a concept like density. We tell students how we define the value of this quantity, but a true understanding of this concept requires seeing that density does not depend on the sample size. It depends only on T, p, and composition. Students must also understand why this follows from the additivity of mass and volume: The density is characteristic of the substance and its state—not of the sample size.

The basic ideas on which the "extensive/intensive" classification is based are

- the additivity of a property with respect to parts of a system
- the constancy of a property in all parts of the system at equilibrium

The idea of additivity of the mass and volume of a sample is best explored by the "discovery lab" method using simple systems like water or a solution of sodium chloride. Students can then be led to explore how the ratio of mass to volume depends on sample size, temperature, and concentration of sodium chloride. The constancy of this ratio then becomes a "law", and problems involving this law can be introduced even before the term density is introduced. Students should also be invited to measure the temperature at various points in the system and contrast this with the results they obtained with mass and volume.

Hypothetical Experiments

Unfortunately, my students have not had such a discovery course in high school, and lack of time has kept me from developing the subject this way. I do the next best thing: I discuss the relevant ideas in terms of hypothetical experiments and try to elicit responses from students as to the results they think they would obtain.

Students have no difficulty with the additivity of mass and volume. I then have them consider the additivity of numbers of particles and amounts (no. of mol). The effect of increasing (doubling, trebling, etc.) the size of a sample (system) on the ratio of two such additive properties is considered. Students are also invited to consider how they would verify that a solution is homogeneous. These consid-

erations lead them to the concept of properties that have the same value everywhere. Specific examples of such properties are considered.

I try to reinforce the idea that the ratio of two extensive properties is independent of sample size. One way is to introduce problems long before formally introducing the relevant intensive properties like concentration and molality.

My experience in teaching these ideas at the freshman level is limited, but I have consistently used this approach in the physical chemistry course at the junior level. The treatments at both levels have many ideas in common, but at the junior level I am able to give a systematic treatment at the beginning of the course because students are already familiar with many of the concepts.

My goal is to show how these ideas will help them do the following.

- correlate a large number of properties
- understand the rules for describing a system
- check the consistency of equations
- understand the physical significance of equations

Calculating Intensive Quantities

Students often have difficulty calculating intensive quantities or deriving theoretical expressions for them. Intensive quantities are by definition independent of sample size. Thus, they can be expressed completely in terms of other intensive quantities. The ideal gas equation is a good yet simple way to show this.

Exercises I have students try include

- obtaining the expression for the concentration of an ideal gas in terms of T and p
- obtaining the expression for the density of an ideal gas

Another good exercise is the derivation of the expression for the average molar mass of a mixture. They know that it is an intensive quantity, but can they express it entirely in terms of other intensive quantities? More difficult examples are expressing molalities in terms of concentrations and vice versa.

Choosing Any Convenient Size

I stress that because intensive properties are independent of sample size, we may consider any convenient sample size. To illustrate some of these ideas I work problems of the following type, emphasizing how our knowledge of intensive and extensive properties can guide us.

Problem

- A 0.4332 M solution of $MgCl_2$ at 20 °C and 1 atm has a density of 1.0311 g/cm^3.
  Calculate the molality of magnesium chloride.

Solution

Because molality is an intensive property, it is independent of sample size. To calculate it we can consider a sample in the prescribed state but of any extent. We may choose a convenient extent for the sample from one of the following: mass of solution, mass of magnesium chloride, volume of solution, etc.

A natural choice seems to be the volume of solution because both concentration and density refer to volume of solution. We take a sample of solution of volume 1 L. For this sample we get the following.
From

$$n_i = c_i \times V$$

we get

$$n(MgCl_2) = 0.4332 \text{ mol}$$

and from

$$W = d \times V$$

we get

$$W(\text{solution}) = 1.0311 \times 1000 \text{ g}$$

By definition, molality is given by

$$m(MgCl_2) = \left(\frac{n(MgCl_2)}{\text{mass of solvent}} \right)_{\text{any sample}}$$

Thus, we need to know the mass of solvent.

Because we appear to have exhausted all the relationships between extensive quantities, we need another source of information concerning mass, so we try the law of conservation of mass.

$$\text{Mass of solution} = \text{mass of } H_2O + \text{mass of } MgCl_2$$

The mass of solute can be calculated from the amount. From

$$W_i = n_i \times M_i$$

we get

$$W(MgCl_2) = 0.4332 \text{ mol} \times \frac{95.2 \text{ g}}{\text{mol}} = 41.2 \text{ g}$$

The mass of water is thus

$$1031.1 \text{ g} - 41.2 \text{ g} = 989.9 \text{ g} = 989 \times 10^{-3} \text{ kg}$$

Therefore

$$m(MgCl_2) = \frac{0.4332 \text{ mol}}{0.989 \text{ kg}} = \frac{0.438 \text{ mol}}{\text{kg}}$$

I stress how important it is for students to show their reasoning, as in the above example, and I give them credit for this. This minimizes working by rote memory.

Single- and Multistep Calculations

The idea that the extensive properties of a phase are directly proportional to one another is, when coupled with definitions of intensive properties, a very fruitful one in mapping out the strategy for solving a problem. The importance of mapping out a path has been stressed (9). The book by Yi-Noo Tang (10) is one of the few solutions manuals that I have seen that does an excellent job encouraging the student always to write out a solution path.

Using A Strategic Map

The following illustrates how I help students find their way through a multistep problem.

Problem

- Calculate the amount of H_2SO_4 in 2 L of a solution of sulfuric acid in which the mass percentage of H_2SO_4 is 96.4% and the density is 1.84 g/mL.

Solution

Summarizing the data, we have

$$V(\text{solution}) = 2 \text{ L}$$

$$\frac{W(H_2SO_4)}{W(\text{soln})} = \frac{96.4}{100}$$

$$\rho(\text{soln}) = 1.84 \frac{\text{g}}{\text{mL}}$$

$$n(H_2SO_4) = ?$$

Because $n(H_2SO_4)$ is an extensive quantity, it can be calculated from another extensive quantity. We have been given the extensive quantity $V(\text{soln}) = 2$ L. If we knew the ratio $n(H_2SO_4):V(\text{soln})$ we could solve the problem.

To get this ratio we consider another sample. Size does not matter, but the data suggests that we fix either the

mass or volume of the solution. Let us take 100 g of solution. For this sample we must calculate the amount of sulfuric acid and the volume of the solution. I have students draw a rough circle to represent their sample and get them to calculate all extensive properties associated with this system.

From the assumption we get $W(\text{soln}) = 100$ g. The task is of course to get the amount of sulfuric acid and the volume of the solution. From the physical interpretation of mass percentage, we have $W(H_2SO_4) = 96.6$ g.

Thus,

$$n(H_2SO_4) = \frac{96.6 \text{ g}}{98.07 \frac{\text{g}}{\text{mol}}} = 0.985 \text{ mol}$$

We now need the volume of solution. The definition of density gives

$$V(\text{soln}) = \frac{100 \text{ g}}{1.84 \frac{\text{g}}{\text{mL}}} = 54.3 \text{ mL}$$

Using the constancy of $n(H_2SO_4)/V(\text{soln})$, we now have

$$\frac{n(H_2SO_4, 2\text{-L sample})}{2 \text{ L}} = \frac{0.985 \text{ mol}}{54.3 \times 10^{-3} \text{ L}}$$

We can also do this by considering just one sample. Here again we make use of the fact that the extensive $n(H_2SO_4)$ can be calculated from the extensive $V(\text{soln})$. But we don't know a relationship that relates these two directly. Obviously, we have to do this in several steps. How do we proceed?

Let us try $W(H_2SO_4)$. This would require the molar mass of sulfuric acid, which is of course known. Now too, there does not seem to be a direct relationship between $W(H_2SO_4)$ and $V(\text{soln})$. As a possible next step, the data on mass fraction suggests the extensive quantity $W(\text{soln})$.

Are we home? Yes, of course, since $W(\text{soln})$ and $V(\text{soln})$ are related by the density of the solution. The strategy can be mapped out as below.

$$n(H_2SO_4) \leftarrow W(H_2SO_4) \leftarrow W(\text{soln}) \leftarrow V(\text{soln})$$

The actual calculation can be carried out in separate steps.

- $W(\text{soln})$ from $V(\text{soln})$ using the density
- then $W(H_2SO_4)$ from $W(\text{soln})$ from the mass percentage
- lastly, the required quantity $n(H_2SO_4)$ from $W(H_2SO_4)$ using the molar mass of sulfuric acid

An alternative method that some might prefer uses one step. To generate a one-line relationship we use

$$a = \frac{a}{b} \times \frac{b}{c} \times c \ldots$$

The motivation behind this step is our knowledge that ratios of extensive properties are intensive properties.

The strategic map yields the following.

$$n(H_2SO_4) = \frac{n(H_2SO_4)}{W(H_2SO_4)} \times \frac{W(H_2SO_4)}{W(\text{soln})} \times \frac{W(\text{soln})}{V(\text{soln})} \times V(\text{soln})$$

$$= \frac{1}{M(H_2SO_4)} \times \frac{96.4}{100} \times \rho(\text{soln}) \times 2 \text{ L}$$

where we have used both the density and the definition of the molar mass.

Summary of Problem-Solving Strategy

We are working with quantities, not units, and the starting point in the generation of the map is the required ex-

tensive quantity—the amount of sulfuric acid. Mapping out the path is an essential step in the calculation, and the student should be expected to write it out explicitly. No "mental" steps are involved, and the student is forced to think of relationships between quantities and the definitions of the associated intensive quantities.

A Chart of Relationships

A chart (see the figure) giving the interrelationships between the various intensive quantities is very helpful in mapping out one or more strategies for solving a problem. By using this chart, the student learns to think in terms of quantities and relationships—not in terms of units and the manipulation of units. The student can also map out a path for the solution to a problem even when there are no actual numbers involved.

A major difficulty for the students, especially the weaker ones, is that they cannot always remember the various relationships. There is a definite improvement in their performance if they have the chart of relationships in front of them; a permanent improvement will depend on the students' willingness to memorize the relationships.

Below we use this chart to map out a solution to two different problems in which no numbers are involved, one involving an extensive quantity and another an intensive quantity.

Finding an Extensive Quantity

Problem

- Determine the amount of a solute i in a given volume of solution, when the concentration of solute i is not known. What other information would be required to enable us to calculate $n(i)$?

Solution

The chart tells us that $n(i)$ is related to $V(\text{tot})$ by $c(i)$. (All three sit on the same circle.) However, we do not know $c(i)$.

We must take an alternative route. An adjacent circle of relationship involves $W(\text{tot})$ and $d(\text{tot})$, which takes us to
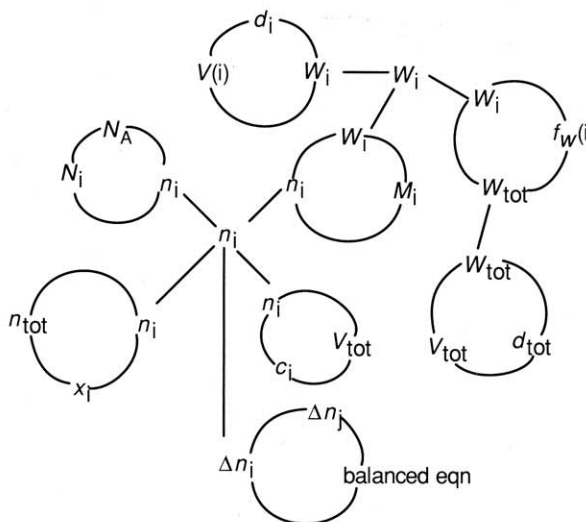

Chart of Relationships. Circles connect values that are related to each other by simple relationships. (The bottom circle shows that a change in the amount of a species, $\Delta n(i)$, is related to the change in another species, $\Delta n(j)$, by the coefficients that balance the reaction equation.) Lines show interrelationships that can be used to strategically map out paths for problem solving. (Because $n(i)$ is found on five circles, it is often used to obtain one of the other values found on the five circles. The path depends on the information given.)

the next circle of relationship involving $W(i)$ and $W(\text{tot})$ through the mass fraction $f_w(i)$. Having come to $W(i)$, we find that it is easy to calculate $n(i)$.

Finding an Intensive Quantity

Problem

- Calculate the concentration $c(i)$ of a solute i from its molality $m(i)$ in a solution containing only one solute i. What further quantities are required?

Solution

The first thing to note is that the relationship must involve intensive quantities only, because an intensive quantity can be expressed completely in terms of intensive quantities. Also we can consider any extent in deriving the relationship.

We must go from the circle of relationship involving $c(i)$, $n(i)$, and $V(\text{tot})$ to the one involving $m(i)$, $n(i)$, and $W(\text{solvent})$. We wish to establish a connection between $c(i)$ and $m(i)$. Because $n(i)$ is common to both circles, we must connect $W(\text{solvent})$ with $V(\text{tot})$. We can go through $V(\text{tot})$ to $V(\text{tot})$, $d(\text{tot})$, and $W(\text{tot})$.

Can we connect $W(\text{solvent})$ and $W(\text{tot})$? Yes, through the law of conservation of mass

$$W(\text{tot}) = W(\text{solvent}) + W(i)$$

where $W(i)$ is given by

$$W(i) = n(i) \times M(i)$$

To actually derive the relationship we first write down both definitions.

$$c(i) = \frac{n(i)}{V(\text{tot})}$$

and

$$m(i) = \frac{n(i)}{W(\text{solvent})}$$

We now have

$$c(i) = \frac{n(i)}{V(\text{tot})} = \frac{n(i)}{\dfrac{W(\text{tot})}{d(\text{tot})}} = \frac{n(i) \times d(\text{tot})}{W(\text{solvent}) + n(i)M(i)}$$

Are we home? Not quite. We must express the RHS in terms of $m(i)$, which is related to $W(\text{solvent})$ and $n(i)$. One way to do this would be to write $W(\text{solvent})$ in terms of $n(i)$ and $m(i)$. Then simplify. Because

$$m(i) = \frac{n(i)}{W(\text{solvent})}$$

it would be quicker to divide the numerator and denominator by $W(\text{solvent})$.

$$c(i) = \frac{m(i) \times d(\text{tot})}{1 + M(i) \times m(i)}$$

Thus, we need to know the density of the solution and the molar mass of i.

Conclusion

Though I do not have objective data comparing the approach outlined above with other approaches, from talking with my students I get the impression that they find the concepts of intensive and extensive properties very helpful in several ways.

- in understanding the physical significance of equations
- in correlating various properties
- in working out a strategy for problem solving

Recognizing that a quantity is extensive sometimes gives them a valuable clue that they had missed. This enables them to try the general laws applicable to extensive properties. Their main difficulty is that they (especially the freshmen) are still thinking in the "dimensional analysis" mode, and it takes effort to grow.

These concepts are fundamental and may very well be teachable even at the school level. The idea of additivity of certain properties and constancy of others is easily explored in the laboratory and may improve concept formation.

The main objective of the approach has been to provide a general conceptual framework for students—not a problem-solving method. However, students can use these concepts with the different problem-solving methods. All approaches would benefit from some emphasis on the correlational power of these concepts.

Literature Cited

1. Landsberg, P. T. *Thermodynamics and Statistical Mechanics*; Oxford University: Oxford, 1978; p 79.
2. Whitten, K. W.; Gailey, K. D.; Davis, R. E. *General Chemistry with Qualitative Analysis*; Saunders College: NY, 1988; p 5.
3. Kotz, J. C.; Purcell, K. F. *Chemistry and Chemical Reactivity*; Saunders College, NY, 1987; p 11.
4. Holtzclaw, Jr., H. F.; Robinson, W. R.; Odom, J. D. *General Chemistry*; D. C. Heath: Lexington, 1991; p 6.
5. Bodner, G. M.; Pardue, H. L. *Chemistry: An Experimental Science*; John Wiley: NY, 1989; p 26.
6. Dierks, W.; Weninger, J.; Herron, J. D. *J. Chem. Educ.* **1985**, *62*, 839.
7. Gold, M. *J. Chem. Educ.* **1988**, *65*, 780.
8. Tykodi, R. J. *J. Chem. Educ.* **1982**, *59*, 557.
9. Kean, E.; Middlecamp, C. H.; Scott, D. L. *J. Chem. Educ.* **1988**, *65*, 987.
10. Tang, Y.-N.; Keeny-Kennicutt, W. *Solutions Manual to Accompany General Chemistry by Whitten, Gailey and Davis*; Saunders College: NY, 1987.