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ON DERIVED CONCEPTS OF MATERIAL[1]

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THE previous[2] treatment of the concept of quantity of material leads to some derived material concepts, which will be dealt with below.

ABSOLUTE† QUANTITIES AND THE CORRESPONDING RATIOS

Absolute material quantities—An extensive absolute material quantity of a definite quantity of material is a quantitative property proportional to the latter, with the dimension of the relevant magnitude. *Tables I* and *II* give examples.

Table I. Absolute atomic and molecular quantities

Name of quantity	*Symbol*	*Numerical magnitude*‡	*Dimension*
The mass of the H atom	$m_{\text{H-atom}}$	$1{\cdot}6 \times 10^{-24}$ g	[Mass]
Mass of the H_2O molecule	$m_{H_2O\text{-molecule}}$	3×10^{-23} g	[Mass]
Mean heat of vaporization of 1 molecule of H_2O	$L_{H_2O\text{-molecule}}$	$-1{\cdot}6 \times 10^{-20}$ g-cal	[Energy]
Boltzmann constant	k	$1{\cdot}38 \times 10^{-23}$ joules per °C	[Energy/ Temperature]
Charge on the electron	e	$1{\cdot}6 \times 10^{-19}$ coulomb	[Charge]

The inequality of the atomic and the corresponding molar absolute quantities appears in the relationships:

$$R = \mathcal{N}_L.k \quad \text{and} \quad F = \mathcal{N}_L.e \quad (\mathcal{N}_L = \text{Avogadro's number} = 6{\cdot}02 \times 10^{23}).$$

Hence it is essential to attach to the name of the corresponding absolute quantity the name of the quantity of material envisaged, i.e. whether it is one atom or molecule, or a mole.

The symbol must refer clearly to the magnitude it is intended to represent. There is a standard international usage which covers this for the molar (or equivalent) absolute quantities F, R, C_p, and for the atomic (or molecular) absolute quantities e and k there is no confusion. But in other cases the relevant subscripts must be attached, as has been done in *Tables I* and *II*. It must be remembered that nowadays the symbol 'H_2O' may be taken by the reader to mean one molecule or one mole of water, and must be qualified to avoid confusion. In general the material symbol itself is used, as far as this is necessary for clarity, in the text, but not in the symbols for quantities.

† Absolute is used here only as a means of differentiation from a ratio.
‡ Rounded off, not strictly accurate.

Table II. Molar absolute quantities (or absolute mole quantities)

Name of quantity	*Symbol*	*Numerical value*†	*Dimension*
Molar vol. of water	$v_{\text{mole } H_2O}$	18 ml (cm^3)	[Volume]
Molar mass of H	$m_{\text{mole H}}$	1 g	[Mass]
Molar heat capacity of H_2O	C_{p,H_2O}	18 g-cal/°C	[Energy/Temperature]
Affinity of formation of 1 mole H_2O	A_{H_2O}	52 kcal	[Energy]
Molar gas constant	R	8·3 joules/°C	[Energy/Temperature]
Faraday (Equivalent charge)	F	96,500 coulomb	[Charge]
Molar Transenergy,† ='Transenergy Content' at T°K	E_i	$\begin{cases} (T) \times 12{\cdot}46 \text{ joule} \\ (T) \text{ Boltz} \end{cases}$	[Energy]

The situation described can be put into everyday terms somewhat as follows:

$$1 \text{ packet of pencils} = 12 \text{ pencils}$$

with the extensive absolute quantities

$$1 \text{ pencil packet-mass: } m_{\text{packet}} = 72 \text{ g (Dimension of [Mass])}$$

$$1 \text{ pencil-mass: } m_{\text{pencil}} = 6 \text{ g (Dimension of [Mass])}$$

whence the relation $m_{\text{packet}} = 12 m_{\text{pencil}}$ so that $m_{\text{packet}} \neq m_{\text{pencil}}$.

The corresponding ratios—The 'intensive' characteristics (constants) of quantitative properties of definite substances, having the dimension of [Quantity]/[Quantity of material] are the 'mole-based' or 'atom-based' ratios, of which a number are given in *Table III.*

Table III. Mole- and atom-based quantities

Name	*Symbol*	*Mole-based value*‡	*Atom-based value*
Heat of vap'n of H_2O	$L^*_{H_2O}$	−9·7 kcal/mole	$= -1{\cdot}6 \times 10^{-23}$ kcal/molecule
Heat of combustion of C	W^*_C	94 kcal/mole	$= 16 \times 10^{-23}$ kcal/molecule
Integral heat of dilution of NaCl in water from small initial concentration c.	$V^*_{c,\text{NaCl}}$	−1 kcal/mole NaCl	$= -1{\cdot}6 \times 10^{-24}$ kcal/molecule NaCl
General gas constant	R^*	8·3 joule/mole × degree	$= 1{\cdot}38 \times 10^{-23}$ joule/molecule × degree
Faraday constant	F^*	96,500 coulomb/equivalent	$= 1{\cdot}6 \times 10^{-19}$ coulomb/univalent cation

† Because of the practical equivalence of a molar absolute quantity and a—somewhat more abstract—corresponding mole-based ratio, the translational energy content in 1 mole of an ideal gas was called the 'Transenergy content' (*Z. Elektrochem.* 57 (1953) 385). The above exposition shows that the occasionally expressed objection that the ratio formulation [Energy/mole] was not chosen (CLUSIUS, K., *Z. Elektrochem.* 57 (1953) 857) cannot be sustained. I did not make a proposal in my paper, but a reference to some interesting consequences. The ideas themselves, as stated, go back very largely to E. Bodea. Also, reference should not be made to a dimension of [Degree] but to one of [Temperature]. Clusius's suggestion that the temperature should be defined as [Energy]/[Entropy] is unfortunate, because there is no fundamental dimension [Entropy]. The best that could be done would be to attribute to entropy the same dimension as the Boltzmann constant, on the basis of the Boltzmann equation. The dimension proposed by Clusius for temperature would thus lead to the result that the temperature has the dimension of [Temperature].

‡ Rounded off, not strictly accurate.

The equivalence of mole- and atom-related quantities is characteristic: if we put: $1{\cdot}38 \times 10^{-23}$ joule/degree.molecule$\equiv k^*$ and $1{\cdot}6 \times 10^{-19}$ coulomb/univalent cation$\equiv e^*$ we would then have:

$$R^* = k^* \quad \text{and} \quad F^* = e^*$$

In chemistry, for experimental reasons, mole-based ratio quantities are preferred for many purposes.

For this reason, the name of the ratio quantity should not contain the name of the material particle or quantity of material employed, be it atom or mole, just as it would not be possible or usual to write of a 'litre-density' of water, because this can be expressed in kg/litre. The expression found in the literature, mole-volume (generally expressed as molar volume) can thus only refer to the relevant absolute quantity, about 18 cm^3 for 1 mole of water, and not to the ratio, 18 cm^3/mole water.†

The same obviously applies for the general symbol for such a ratio expression. To reduce the number of symbols which have to be used to the minimum possible, a superscript asterisk (*) has sometimes been added to the usual symbol for an absolute quantity, to denote a symbol for the corresponding general ratio.

The different methods of applying absolute quantities and ratios in equations—The need to differentiate between absolute quantities and ratios is specially pronounced in equations, as will appear from the two examples given below.

In calculating a magnitude of any quantity of a pure substance, e.g. the mass m of $\mathcal{N}$ atoms $= n$ moles of Ag, two different equations are obtained with absolute quantities:

$$\text{with the atom-mass } m_{\text{at}} \qquad m = \mathcal{N}.m_{\text{at}}$$

$$\text{with the mole-mass } m_{\text{mole}} \qquad m = n.m_{\text{mole}}$$

The same applies for the volume V of an ideal gas:

$$V = \mathcal{N}kT/p \quad \text{and} \quad V = nRT/p$$

or for the charge of $\mathcal{N}$ potassium ions $K^+ = n$ moles of K^+

$$q = \mathcal{N}e \quad \text{and} \quad q = nF$$

The opposite applies for the molar volume: $v^i = V/n$ and for the partial molar volume $v_i = \partial V/\partial n_i$ both having the dimensions of [Volume].

Using the corresponding ratios, only one pure quantity equation exists: $m =$ quantity of material $\times$ (mass/quantity of material). For these ratios e.g. $1{\cdot}6 \times 10^{-24}$ g atom or 1 g/mole H can be used, and for the quantity of material, $\mathcal{N}$ atoms H or n moles H can be inserted:

$$m = (\mathcal{N} \text{ atoms H}) \times 1{\cdot}6 \times 10^{-24} \text{ g/H atom} = (n \text{ moles H}) \text{ g/mole H}$$

$$= \mathcal{N} \times 1{\cdot}6 \times 10^{-24} \text{ g} = n \times 1 \text{ g}.$$

Similar relationships apply for mixed phases. Thus for the mass of a mixed phase there are several equations in absolute units:

$$m = \Sigma N_i.m_{\text{at } i} \quad \text{and} \quad m = \Sigma n_i.m_{\text{mole } i}$$

† Objections to 'molar quantities' (POHL, R. W. *Z. phys. Chem.* 202 (1953) 117) occasionally expressed establish common ground with the objection to the dubbing of actual ratios and even of mole-based quantities as molar quantities. Moreover, the mole concept is of such predominant importance in chemistry as a macroscopic measure of quantity of material, that it would be inconvenient for the chemist to renounce 'molar absolute quantities' and other applications of this measure of quantity of substance.

but only one equation with the corresponding ratios:

$$m = \Sigma \text{ quantity of material } i \times (\text{mass/quantity of material } i).$$

The calculation of an (absolute) reaction quantity is even more important for chemistry. With material absolute quantities and the relevant formula-mole numbers ν_i or formula-molecule numbers π_i several different forms of equations are obtained again: e.g. for the reaction volume:

$$V = \Sigma \nu_i v^i \quad \text{and} \quad V = \Sigma \pi_i \varphi_i N_L$$

with the dimension of [Volume]; v^i is the mole volume and φ_i the corresponding molecule volume. But there is only a single pure quantity equation:

$$V = \Sigma \Delta St_i (\text{volume/quantity of material } i)$$

when the corresponding ratio volume/quantity of material and the relevant expressions

$$\Delta St_i = \nu_i . \text{mole } i = \pi_i . \text{molecule } i$$

are used, expressing the variations of the quantities of material i participating.

This method of calculation of a reaction quantity has not so far been common practice in chemistry, but is recommended for practical trial because of the advantage of its general validity.

Summarizing it results that, particularly in view of their differing forms of use in equations, absolute quantities must be strictly differentiated from the corresponding ratios. This applies particularly if in both the same units and species occur or are specified, e.g. kcal and moles in the statements:

'the molar heat of vaporization of water is 9·7 kcal'

and 'the heat of vaporization of water is 9·7 kcal/mole'

because the number used is the same in both cases, 9·7. The striking similarity found in this particular case is the reason why often, and in cases unconsciously, transition is made from one of the two modes of expression to the other, and frequently the one is confused with the other, without the author being aware at all that they must be differentiated. If they are kept strictly apart, both modes of expression can be used without confusion; the ratio 9·7 kcal/mole of water has the advantage that the quantity of material dealt with, here 1 mole of water, can be expressed in a shorter form, so that this mode of form is often preferred in quoting individual values in texts, in tables or in graphs. On the other hand the absolute value is doubtless simpler and less abstract, therefore easier to understand and more capable of visualization. In any case it is important that when these expressions are applied in equations, the correct and suitable choice is made.

This emerges even in everyday speech. Thus often a quantity, e.g. the velocity $c = 80$ km/hour $= 22$ m/sec is depicted in terms of one of the two corresponding absolute quantities: the distance covered per hour, 80 km, or the distance covered per second, 22 metres; whereas the two ratios are

equal, the absolute values are not; one is 3,600 times the other. Further examples of depicting ratios in terms of absolute quantities derived from everyday speech are litre weights, gram prices, daily receipts, monthly income, yearly death rate.

CONCENTRATION DATA

Two kinds of material concentration unit can be differentiated, in analogy with the foregoing.

Number-based concentration—Examples of this, having the dimension of $[\text{Volume}]^{-1}$, are:

$$\text{atom number concentration } c_{\text{at}} = \mathcal{N}_{\text{at}}/V_{\text{soln}};\ \text{e.g. } 6 \times 10^{22}/\text{litre}$$

$$\text{mole number concentration } c_{\text{mole}} = n_{\text{mole}}/V_{\text{soln}};\ \text{e.g. } 0{\cdot}1/\text{litre}$$

The inequality of atom-number and mole-number concentration statements for a given mixed phase is characteristic:

$$c_{\text{at}} (\equiv \mathcal{N}_{\text{at}}/V_{\text{soln}}) = \mathcal{N}_L . c_{\text{mole}} (\equiv \mathcal{N}_L . n_{\text{mole}}/V_{\text{soln}})$$

e.g.

$$6 \times 10^{22}/\text{litre} = \mathcal{N}_L \times 0{\cdot}1/\text{litre}\ (\mathcal{N}_L = \text{Avogadro's number}).$$

Both the names and the symbols for the number-based concentration data must state clearly the basis, i.e. here the atom or mole, to avoid confusion.

Material-quantity concentration—This has the dimension of [Quantity of material]/[Volume]:

$$c^* = \text{quantity of material}/V_{\text{soln}} = \mathcal{N} \text{ atoms}/V_{\text{soln}} = n \text{ moles}/V_{\text{soln}}$$

e.g. $c^* = 6 \times 10^{22}$ atoms/litre $= 0{\cdot}1$ mole/litre $= 0{\cdot}1$ m.

The equality of 'atom-based' and 'mole-based' material quantity concentration data, is characteristic. Hence the general name and general symbol need not contain any reference to the basis.

Different forms of application of the two kinds of material concentration data in equations—This is again very important. For calculation of the numbers, e.g. of atoms $\mathcal{N}_{\text{at}}$ or moles n_{mole} for a given mixed phase having the volume V there are two different equations if concentrations are number-based:

$$\mathcal{N}_{\text{at}} = V . c_{\text{at}} \quad \text{and} \quad n_{\text{mole}} = V . c_{\text{mole}}$$

Two further equations can be compounded to calculate the charge q of the electricity carried by the $\mathcal{N}_{\text{at}}$ and n_{mole} of univalent ions:

$$q = \mathcal{N}_{\text{at}} . e = e . V . c_{\text{at}} \quad \text{and} \quad q = n_{\text{mole}} . F = F . V . c_{\text{mole}}$$

On the other hand, material-quantity concentrations c^* yield only one equation for the quantity of material:

$$\text{quantity of material } i = V . c^*$$

or for the charge:

$$q_i = \text{quantity of material } i . F^* = V . c^* . F^*$$

in which $F^* = 96{,}500$ coulombs/equivalent $= 1{\cdot}6 \times 10^{-19}$ coulomb/univalent ion.

Conclusion—The two possible methods of expressing material concentration must thus be clearly differentiated from one another. This applies also and particularly if the same volume unit (say litre) and the same portion of material (mole) are used. For in the mole-number concentration $c_{\text{mole}} = 0{\cdot}1$/litre and in the material–quantity concentration $c^* = 0{\cdot}1$ mole/litre, the same number 0·1 appears, known to chemists as the molarity. This similarity occasionally results in writers' going from one mode of expression to the other, and frequently in confusing one with the other, or in being entirely unaware that they must be differentiated.

When these methods of expressing material concentration are kept strictly apart, both are suitable for the unequivocal description of mixed phases. The material–quantity concentration has the advantage of expressing the basis, e.g. the mole, without confusion in a shorter form, whence once again the preference shown for it in original papers, etc. But the number-based concentration is less abstract and therefore easier to visualize. In any case it is important that the right form is employed in equations. Number-based concentrations are used almost without exception for the formulation of chemical equilibrium constants and expressions for reaction rates; the predominant form is the mole number concentration.

THE AVOGADRO 'CONSTANT'

Relation between absolute quantities and ratios—Occasionally there is found a relation between the atomic absolute quantities, e.g.

$$\text{elementary charge } e = 1{\cdot}6 \times 10^{-19} \text{ coulomb,}$$

$$\text{Boltzmann constant } k = 1{\cdot}38 \times 10^{-23} \text{ joules/°C}$$

and the corresponding ratios,

$$\text{Faraday constant } F^* = 96{,}500 \text{ coulombs per equivalent}$$

$$\text{General gas constant } R^* = 8{\cdot}3 \text{ joules/°C. mole}$$

of the form:

$$F^* = \mathcal{N}_L^* . e \quad \text{and} \quad R^* = \mathcal{N}_L^* . k,$$

giving the Avogadro 'Constant'

$$\mathcal{N}_L^* = 6 \times 10^{23}/\text{mole.}$$

(Here apparently analogy with the simpler and more graphical relations:

$$F = \mathcal{N}_L . e \quad \text{or} \quad R = \mathcal{N}_L . k$$

between the corresponding absolute quantities is involved where the simple Avogadro number $\mathcal{N}_L = 6{\cdot}02 \times 10^{23}$ occurs).

However, there are objections to the first-named procedure. For one thing it is at least not particularly consistent, to use absolute quantities on the atomic, and ratios on the molar, scale. Again, the 'Constant' is not a constant, but varies from one substance to another, because the mole in the denominator is, e.g. for He, quite different from that for any other substance. Moreover, we generally meet with the equation $pV = nRT$, in which, as expounded above, doubtless the molar gas constant $R = 8{\cdot}3$ joules/°C occurs

but not the ratio $R^* = 8{\cdot}3$ joules/°C.mole. If R^* is used, to be dimensionally correct the equation must run:

$$pV = \text{quantity of material} \,.\, R^* T$$

The occasional equating of mole and molar mass—We sometimes find it said that 1 mole of a pure substance should be equal to the corresponding molar mass, e.g. that 1 mole He $= m_{\text{mole He}} = 4$ g. The objection to this already voiced[2] is specially significant, if at the same time the so-called Avogadro 'Constant' is used. We should then have for He, since $m_{\text{mole He}} = 6 \times 10^{23} m_{\text{at He}}$

$$N_L^* = 6 \times 10^{23}/\text{mole He} = 6 \times 10^{23}/m_{\text{mole He}}$$
$$= 1/m_{\text{at He}}$$

The Avogadro 'Constant' N_L^* would then be simply the reciprocal of the relevant atomic mass, again not a true constant of nature, independent of the substance, but merely a constant for a particular substance, with the dimension of $[\text{Mass}]^{-1}$. It can hardly be claimed that the putting of 1 mole = 1 mole-mass is a simplification; this introduction of an individual mass unit for each substance has been objected to frequently on other grounds.

The occasional equating of 1 mole with 6×10^{23}—If this were to be inserted in the expression for the Avogadro 'Constant', we should obtain:

$$N_L^* = 6 \times 10^{23}/\text{mole} = 6 \times 10^{23}/6 \times 10^{23} = 1$$

an impossible result, which indicates the impossibility of equating 1 mole with 6×10^{23}. The same paradoxical conclusion would be arrived at, if the occasionally given definition of the Avogadro 'number' $N_L = 6 \times 10^{23}$ molecules/mole is tested. Since 1 mole $= 6 \times 10^{23}$ molecules, we should get unity for this Avogadro 'number' N_L!

REFERENCES

[1] LANGE, E. *Phys. Bl.* 10 (1954) 504

[2] LANGE, E. 'Das Mol—ein Stoffmengenmass' *Phys. Bl.* 10 (1954) 259. This contains references to earlier literature.