

NORMALIZATIONS OF THERMODYNAMIC PROPERTIES AND SOME IMPLICATIONS FOR GRAPHICAL AND ANALYTICAL PROBLEMS IN PETROLOGY

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ABSTRACT. Petrologic problems may be analyzed using any of a variety of possible choices of units. Although gram-formula units (moles) are commonly used, other units of quantity are more appropriate for many applications. Gram-atom units offer the numerical simplicity of gram-formula units and have the advantage of being conservative. A conservative unit of quantity is one for which the sum of the units of reactants equals the sum of the units of products in a chemical reaction. For many graphical problems, a conservative unit of quantity, such as gram-atom or mass units, should be used. Since gram-formula units are not conservative, the lever rule can lead to incorrect results when applied to composition axes based on units of gram-formula percent. Similarly, the graphical evaluation of Gibbs energy relationships and chemical potentials on energy-composition diagrams is facilitated by the use of a conservative unit of quantity. Thermochemical data show consistent patterns when normalized on a gram-atom basis, whereas with gram-formula units they do not. Mean atomic entropies of formation are so similar for all complex oxides that they may be predicted with precision. This is partly due to the dominance of the entropy term for gaseous oxygen, when the elements in their stable form are chosen as the standard state. In detail, mean atomic entropies of formation show a positive correlation with mean atomic weight for all silicates, a relationship that can be used to correct entropy estimates for mass effects.

UNITS OF QUANTITY

Mass units.—Traditionally, the amount of a mineral or other solid compound has been expressed in units of mass. Mass is a logical choice for a unit of quantity, since it is easily measured with high precision. J. Willard Gibbs (1928) used mass exclusively as the unit for chemical components, developing the important relations of heterogeneous equilibria in terms of specific (mass reduced) and partial specific quantities. Mass units have the important property of being conserved in any chemical reaction, which is convenient for bookkeeping and for many graphical applications. In other words, the sum of the masses of the reactants is equal to the sum of the masses of the products. Mass is also the unit of quantity directly measured in many instances. Unfortunately, the use of mass units has the disadvantage of obscuring the relatively simple stoichiometry of most minerals, and therefore cumbersome numbers are required to balance chemical reactions. For these reasons mass units, which are widely used in the experimental literature, have been largely neglected in most theoretical applications.

Gram-formula units.—Gram-formula units (moles) offer obvious advantages for any discussion of chemical equilibria. Because of the fact that atoms combine in simple proportions, chemical reactions are easily balanced in terms of gram-formula units and integer coefficients. However, gram-formula units are *not* conserved in chemical reactions. In other words, the sum of the number of moles of reactants is generally not equal to the sum of the number of moles of products. While this feature is not

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overly troublesome, it is indicative of the problems implicit in the use of gram-formula units. Gram-formula units are generally preferred over mass units because they involve quantities proportional to the number of atoms in mineral formulas. The problems with gram-formula units arise because the constant of proportionality (number of atoms per formula) is different for each formula.

Gram-atom units.—Gram-atom units have been typically used for applications that involve atom to atom interactions, such as those encountered in the physical interpretation of heat capacity (Debye, 1912). Although their “per particle” quality is attractive, gram-atom units have only rarely appeared in the petrologic literature (for example, Thompson, 1955). Gram-atom units are best defined operationally. To obtain the number of gram-atom units of a mineral, either (1) divide its mass by its mean atomic weight (Birch, 1952, 1961) or, equivalently, (2) multiply its number of gram-formula units by the number of atoms per formula unit. Comparative values of mass units, gram-formula units, and gram-atom units are given in table 1 for some common minerals. Table 2 provides an example of a chemical reaction balanced in terms of each of these choices of units.

Gram-atom units conveniently provide some indication of quantity without reference to mineral formulas, as do mass units. Formulas are thus relegated to their proper role of identifying and giving ratios between the elements involved. For example, there is no need to distinguish between $Mg_2Si_2O_6$ and $MgSiO_3$ when gram-atom units are used. The implications of this fact are clear when reading chemical reactions that have been balanced in gram-atom units (table 2). Seven gram-atoms of Mg_2SiO_4 means two gram-atoms of Mg, one gram-atom of Si, and four gram-atoms of O. One gram-atom of Mg_2SiO_4 means 2/7 gram-atoms of Mg, 1/7 gram-atoms of Si, and 4/7 gram-atoms of O.

Gram-atom units offer an alternative that has many of the advantages of *both* mass units and gram-formula units. Like gram-formula units, gram-atom units are proportional to the number of atoms per formula unit, but unlike gram-formula units, the constant of proportionality is the same for all compounds. Like mass units, gram-atom units are *conservative* (an equal number of units appear on both sides of a balanced

TABLE 1
A numerical comparison of some alternative units of quantity

Mineral	Formula	Gram- Formula Weight	Gram- For- mula Units	Mean Atomic Weight (g)	Gram- Atom Units	Gram- Oxygen Units	Molar Volume (cm ³)	Gram- Cation Units	Gram- Oxide Units
Periclase	MgO	40.311	1	20.156	2	1	11.248	1	1
Forsterite	Mg ₂ SiO ₄	140.708	1	20.101	7	4	43.79	3	3
Clino- enstatite	MgSiO ₃	100.396	1	20.079	5	3	31.47	2	2
Quartz	SiO ₂	60.085	1	20.028	3	2	22.688	1	1

See text for definitions. Data from Robie, Hemingway, and Fisher (1978).

chemical reaction). Unlike mass units, gram-atom units lead to chemical reactions with simple integer coefficients.

Gram-oxygen units.—Another measure of quantity that has some useful applications is the gram-oxygen unit. Gram-oxygen units are obtained from the number of gram-formula units by multiplying by the number of oxygens per formula unit. Like gram-atom units, gram-oxygen units are typically simple whole numbers and are conserved in any chemical reaction (see tables 1 and 2). Gram-oxygen units have the additional advantage of being a first order measure of the volume of most solids in which oxygen is the only major anion (see table 1). This is because most such solids can be represented as nearly close-packed oxygen structures with cations merely occupying voids. Anyone who wishes to convert modal data into an approximate chemical analysis or vice versa (a modal norm) will find gram-oxygen units most helpful. For compounds with major anions other than oxygen, "gram-anion" units may be used. See Walker, Longhi, and Hays (1975) or Thompson (1978) for applications of gram-oxygen units.

Gram-cation units.—The correlation between oxygen and volume led Barth (1948, 1962, p. 62) to propose a "standard cell" for petrographic calculations based on 160 oxygen ions. Barth's normative manipulations, however, were conducted in cation units following the procedures of Niggli (1936). Gram-cation units, which differ by a constant (Avogadro's number) from Barth's cation units, are yet another conservative unit of quantity. Gram-cation units are obtained from gram-formula units by multiplying by the number of cations per formula unit. Barth and Niggli both demonstrate the utility of gram-cation units.

Gram-component units.—Other conservative units of quantity may be defined on the basis of any independent set of chemical components. Perhaps the most straightforward would be gram-oxide units, based on the standard oxide components. The number of gram-oxide units of a mineral is obtained from the number of gram-formula units by multiplying by the sum of the number of oxide formula units in one formula unit of the mineral. Other sets of components may be used to define different gram-component units that are useful for certain applications. It is important to recognize, however, that gram-component units refer to a specific set of components, whereas mass units, gram-atom units, gram-oxygen

TABLE 2

The reaction forsterite = periclase + quartz balanced using various units of quantity. An equal number of units appear on both sides of the reaction written using any of the conservative units; in general, this is not the case for gram-formula units

Gram-formula units:	1	(Mg ₂ SiO ₄) =	2	(MgO) +	1	(SiO ₂)
Mass units:	140.708	(Mg ₂ SiO ₄) =	80.623	(MgO) +	60.685	(SiO ₂)
Gram-atom units:	7	(Mg ₂ SiO ₄) =	4	(MgO) +	3	(SiO ₂)
Gram-oxygen units:	4	(Mg ₂ SiO ₄) =	2	(MgO) +	2	(SiO ₂)
Gram-cation units:	3	(Mg ₂ SiO ₄) =	2	(MgO) +	1	(SiO ₂)
Gram-oxide units:	3	(Mg ₂ SiO ₄) =	2	(MgO) +	1	(SiO ₂)

units, and gram-cation units are independent of any choice of components.

In the following sections we present several petrologic applications for which gram-atom units and other conservative units offer advantages over gram-formula units. We hope that these examples will not only emphasize the important differences between units of quantity but also prompt others to seek additional applications of alternative choices of units.

GIBBS ENERGY-COMPOSITION DIAGRAMS

Standard thermodynamic texts contain a convenient graphical procedure for determining the stable assemblages of phases at a specific temperature and pressure based on the phase compositions (mole fractions) and relative "molar" Gibbs energies of the phases (for example, Darken and Gurry, 1953, chap. 13). The procedure was devised originally by Gibbs (1928, p. 118 and following) who developed it using specific (mass reduced) Gibbs energies and mass fractions (wt percent). The stable mineral assemblages are determined from the Gibbs energies of the phases by using a "tangent line" technique (tangent plane for 3 component systems) to generate tie lines that define the lowest Gibbs energy values for the system (see fig. 1). The use of mole fractions and molar Gibbs energies can lead to incorrect results, if care is not taken to evaluate the meaning of molar Gibbs energy in each instance.

In figure 1 the molar Gibbs energies (kJ/gfu) of the minerals periclase, forsterite, clinoenstatite, and quartz (taken directly from Robie, Hemingway, and Fisher, 1978, for 1000 K and 10^5 pascals) are shown along with chemical compositions plotted in terms of the mole fraction of SiO_2 (see table 3 for notation). Following the tangent line procedure, one would predict from these data that the assemblage forsterite + quartz is more stable at 1000 K than any clinoenstatite-bearing assemblage of the same composition. Of course this result is inconsistent with both petro-

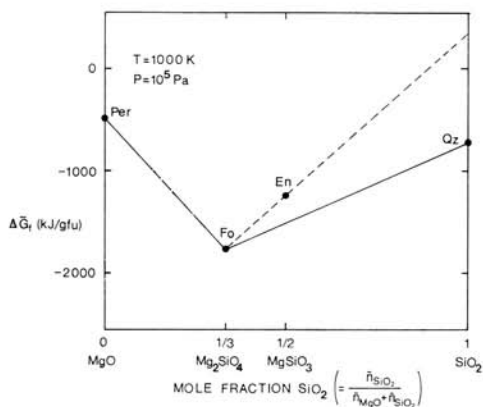


Fig. 1. Gram-formula unit Gibbs energy-composition diagram for the system MgO-SiO_2 . The "stable" mineral assemblages are defined by the solid tie lines, which give the lowest Gibbs energy values. Note that the assemblage forsterite + quartz appears to be stable. See table 3 for notation.

graphic and experimental observations under these conditions, so one is tempted to conclude that one or more of the thermodynamic data are in error. Similarly, if one wishes to evaluate graphically the chemical potential of SiO_2 in the assemblage forsterite + enstatite at 1000 K and 10^5 pascals, one obtains a value greater than that of pure SiO_2 under the same conditions. These incorrect conclusions result from the fact that each of the Gibbs energies is normalized in a different way. In essence, the vertical scale of figure 1 is different for each mineral and depends on the mineral formulas used.

These difficulties may be easily overcome by constructing Gibbs energy-composition diagrams with conservative units. The data of figure 1 are shown in figure 2 with Gibbs energies normalized on a gram-atom basis (mean atomic Gibbs energies) and with compositions expressed as atom fractions (gram-atom percent). Figure 2 is consistent with the observed phase relations. Figure 2 may also be used to evaluate the mean atomic chemical potential (partial gram-atomic Gibbs energy) of *any* component that falls on the composition axis used. For the example of forsterite + enstatite, the mean atomic chemical potential of SiO_2 in that assemblage at 1000 K and 10^5 pascals is -247.109 kJ/gau. Similar benefits would accrue from Gibbs energy-composition diagrams based on any other *conservative* unit of quantity, such as mass units or gram-oxygen units.

TABLE 3
Summary of notation

a_{ij}	= the number of units of component j in one unit of component i
b_{ji}	= the number of units of component i in one unit of component j
C_j	= "old" component j
C'_i	= "new" component i
gau	= gram-atom units
gfu	= gram-formula units
gou	= gram-oxygen units
G	= Gibbs energy
$\Delta\bar{G}_{r,298}$	= Gibbs energy of formation from the elements per gfu at 298 K
$\Delta\hat{G}_{r,298}$	= Gibbs energy of formation from the elements per gau at 298 K
$\Delta\hat{H}_{r,298}$	= enthalpy of formation from the elements per gau at 298 K
J	= joules
kJ	= kilojoules
K	= degrees Kelvin
\bar{M}	= mean atomic weight
\bar{N}_i	= mole fraction of component i
N_D^X	= gram-unit fraction of component D in component X
n_A	= number of units of component A
n_{C_j}	= n units of "old" component C_j
$n_{C'_i}$	= n units of "new" component C'_i
\bar{n}_{SiO_2}	= number of gram-formula units of SiO_2
\hat{n}_{SiO_2}	= number of gram-atom units of SiO_2
n_A^X	= number of units of component A in one unit of component X
P	= pressure
R	= gas constant
$\Delta\bar{S}_{r,298}$	= entropy of formation from the elements per gau at 298 K
$\Delta\hat{S}_{r,298}$	= entropy of formation from the elements per gou at 298 K
T	= temperature

A mole fraction composition axis may be used successfully for these diagrams if the Gibbs energies are normalized on a gram-component basis ("mean molar" Gibbs energies), where the component units are gram-formula units of the endmember components. In the example of figure 1 the endmember components are oxides, so the Gibbs energies should be given in gram-oxide units. This is accomplished by dividing the molar Gibbs energy of each mineral by the sum of the number of moles of the endmember oxides in one gram-formula unit of the mineral (1 for Per and Qz, 3 for Fo, and 2 for En). Alternatively, if all the mineral formulas are normalized to have the same number of gram-component units per gram-formula unit, which commonly means the same number of atoms, cations, or oxygens per mineral formula, then the molar Gibbs energies for these formulas will "automatically" be normalized correctly for use with a mole fraction axis.¹

Either way of using a mole fraction composition axis requires Gibbs energies normalized in a way that depends on the choice of endmember components used. Mean atomic or specific Gibbs energies, however, are independent of any choice of components.

THE LEVER RULE

One of the keystones of the application of phase diagrams is the lever rule, a relationship between the bulk chemical composition of a system and the relative proportions of phases present. The lever rule is based on the principle that "part of it, plus the rest of it, equals all of it" (for example, Darken and Gurry, 1953, p. 316). This principle seems straightforward and, in fact, cannot be faulted for compositions given in any conservative unit of quantity. However, it is relatively easy to obtain incorrect results by applying the lever rule to phase diagrams with compositions expressed in mole percent.

Consider again the minerals forsterite and quartz in the system MgO-SiO₂. Assume for the moment that forsterite and quartz can coexist and that they occur together in a rock with the bulk composition of clinostatite. In figure 3A the compositions of interest are shown using a mole

¹ The fundamental relation (Gibbs, 1928, eq. 96)

$$G = n_A \cdot \left(\frac{\partial G}{\partial n_A} \right)_{n_B} + n_B \cdot \left(\frac{\partial G}{\partial n_B} \right)_{n_A} \quad (P, T \text{ constant})$$

is valid for any choice of unit of quantity for n_A and n_B . To make the equation intensive, both sides are divided by $(n_A + n_B)$ to yield (at constant P and T)

$$\frac{G}{(n_A + n_B)} = \left(\frac{\partial G}{\partial n_A} \right)_{n_B} + \left[\left(\frac{\partial G}{\partial n_B} \right)_{n_A} - \left(\frac{\partial G}{\partial n_A} \right)_{n_B} \right] \frac{n_B}{(n_A + n_B)}$$

For gram-formula units this equation becomes

$$\frac{G}{(\bar{n}_A + \bar{n}_B)} = \bar{\mu}_A + (\bar{\mu}_B - \bar{\mu}_A) \bar{N}_B$$

where $\bar{\mu}_A$ is the partial molar Gibbs energy (chemical potential) for component A. These equations, on which the tangent line procedure is based, serve to define the "mean molar" Gibbs energy $[G/(\bar{n}_A + \bar{n}_B)]$ and to demonstrate further the incorrectness of using molar Gibbs energies in figure 1.

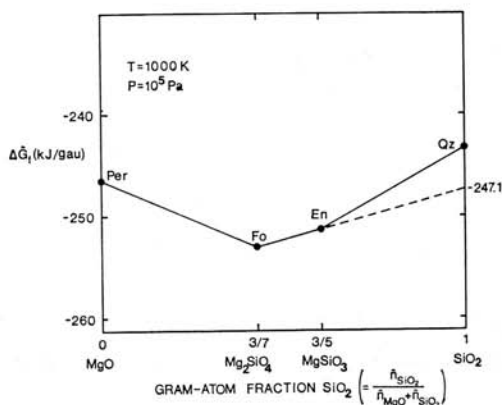


Fig. 2. Gram-atom unit Gibbs energy-composition diagram for the system MgO-SiO₂. The stable assemblages obtained from the tie lines in this figure correctly reflect naturally observed mineral assemblages.

percent composition axis based on the endmembers MgO and SiO₂. Applying the lever rule to figure 3A, one would conclude that for the bulk composition MgSiO₃ the assemblage would be 75 mole percent forsterite and 25 mole percent quartz. However, if the same compositions are shown using a mole percent composition axis based on endmembers Mg₂SiO₄ and SiO₂, one obtains a different result. Applying the lever rule to figure 3B, one concludes that for the bulk composition MgSiO₃, the assemblage would be 50 mole percent forsterite and 50 mole percent quartz. These inconsistent and incorrect results may be avoided if the composition axes are based on a conservative unit of quantity.

The compositions and endmembers of figure 3, A and B, are shown in figure 4, A and B, using gram-atom percent composition axes. Applying the lever rule to either A or B of figure 4, one concludes that for a bulk composition of MgSiO₃, the assemblage would be 70 gram-atom percent forsterite and 30 gram-atom percent quartz. When using conservative

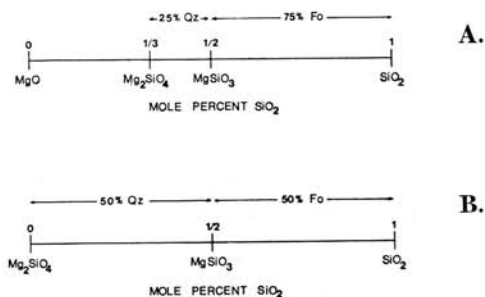


Fig. 3. The relative proportions (mole percent) of quartz (Qz) and forsterite (Fo) are evaluated using the lever rule for a bulk composition of MgSiO₃ and endmembers (A) MgO-SiO₂ and (B) Mg₂SiO₄-SiO₂. For the two choices of endmembers, the lever rule gives two different answers.

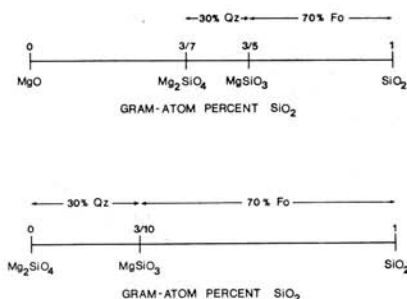


Fig. 4. The relative proportions (gram-atom percent) of quartz (Qz) and forsterite (Fo) are evaluated for the same bulk composition and endmembers as in figure 3, A and B. In this case, however, the answer is the same for both choices of endmembers. units, the choice of endmembers for the composition axes does not affect the lever rule results.

A practical example of the significance of these observations is shown in figure 5. Consider a bulk composition X ($3\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3$) in the system $\text{SiO}_2\text{-Al}_2\text{O}_3$ as it is cooled through the two-phase field of liquid plus mullite. The relative proportions of liquid and solid at 1670°C that would be predicted by applying the lever rule are indicated in figure 5 to be 60 mole percent solid and 40 mole percent liquid. As we shall see, these proportions are not correct for a liquid of formula A ($9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) and a solid of formula B ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$). In this case the most straightforward way to demonstrate the correct relative proportions of liquid (A) and solid (B) relies on a fundamental property of composition axes. By definition, a composition axis based on any unit of quantity gives graphically the fractions of the *endmember components* for any intermediate bulk composition. Therefore, if bulk composition X can be expressed in terms of a composition axis with A and B as endmembers, the desired relative proportions of liquid (A) and solid (B) in figure 5 will be a trivial result. In other words, we need to perform a coordinate transformation from "old" endmembers SiO_2 and Al_2O_3 to "new" end members A ($9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$) and B ($2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_3$).

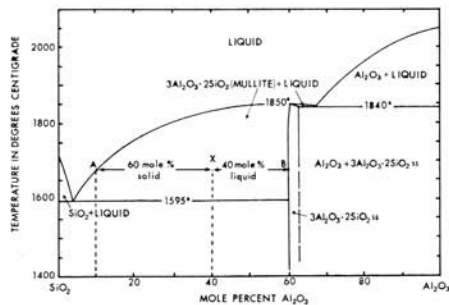


Fig. 5. The system $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Morey, 1964). For the bulk composition X, the lever rule incorrectly predicts an assemblage of 60 mole percent solid and 40 mole percent liquid. The actual proportions of solid and liquid are derived in the text.

In order to transform from one independent set of components to another, the first step is to express the compositions of each of the "new" components (C'_i) in terms of the compositions of the "old" components (C_j). For an n -component system, this requires n stoichiometric equations of the form

$$1 C'_i = \sum_{j=1}^n a_{ij} C_j \quad (1)$$

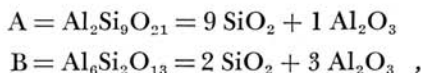
where the coefficients a_{ij} give the number of units of "old" component j in *one* unit of "new" component i .²

Next, the $(n \times n)$ matrix of coefficients a_{ij} is inverted by whatever method is most convenient to give a different $(n \times n)$ matrix of coefficients b_{ji} . Finally, the bulk compositions given in terms of numbers of units of "old" components (n_{C_j}) are converted into bulk compositions in terms of numbers of units of "new" components ($n_{C'_i}$) by equations of the form³

$$n_{C'_i} = \sum_{j=1}^n b_{ji} n_{C_j} \quad (2)$$

where the coefficients b_{ji} give the number of units of "new" component i in one unit of "old" component j . We present these equations in general form because of their usefulness in dealing with problems similar to the one at hand. The basis for these procedures in linear algebra is well known (for example, Anderson, 1974, p. 76; Rabenstein, 1970, p. 161; see, also, Greenwood, 1975).

For the components of interest in the previous example (fig. 5), the stoichiometric relations (1) become



where the unit of quantity is the gram-formula unit (mole) of each component. The matrix of coefficients a_{ij} is therefore

$$\begin{pmatrix} 9 & 1 \\ 2 & 3 \end{pmatrix}.$$

The inverse of this matrix (the b_{ji}) is

$$\begin{pmatrix} 3/25 & -1/25 \\ -2/25 & 9/25 \end{pmatrix}.$$

² Ordinarily, the unit of quantity will be the same for both "old" and "new" components, but it need not be. In fact, the unit of quantity could be different for each component. The procedure is unchanged by the choice of units.

³ The eqs (2) imply a *post-multiplication* of the vector n_{C_j} by the matrix of coefficient b_{ji} . Alternatively, vector n_{C_j} may be premultiplied by the transpose of the matrix of b_{ji} .

The relations (2) for bulk composition X ($3\text{SiO}_2 \cdot 2\text{Al}_2\text{O}_3$) are given by

$$(1/5 \quad 3/5) = (3 \quad 2) \cdot \begin{pmatrix} 3/25 & -1/25 \\ -2/25 & 9/25 \end{pmatrix}.$$

Thus, with the relative numbers of moles of solid ($B = 3/5$) and liquid ($A = 1/5$) in hand, we may proceed to determine the relative percentages of solid and liquid.

$$\bar{N}_{\text{solid}} = \frac{\bar{n}_B}{\bar{n}_A + \bar{n}_B} = \frac{3/5}{1/5 + 3/5} = 3/4$$

There will be 75 mole percent solid ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and 25 mole percent liquid ($\text{Al}_2\text{Si}_9\text{O}_{21}$). These numbers may be contrasted with the 60 and 40 mole percent predicted from the lever rule in figure 5. Clearly the molar proportions one obtains from the lever rule may be significantly in error.

Unfortunately, the molar proportions determined by any correct procedure depend on the choice of formula for the phases involved. If B had been expressed as $3(\text{Al}_6\text{Si}_2\text{O}_{13})$ rather than $\text{Al}_6\text{Si}_2\text{O}_{13}$, the result would have been 50 mole percent liquid ($\text{Al}_2\text{Si}_9\text{O}_{21}$) and 50 mole percent solid ($\text{Al}_{18}\text{Si}_6\text{O}_{39}$). This formula-specific character of gram-formula units is a potential source of misunderstanding that does not exist for conservative units.

Most published phase diagrams are in units of wt percent. Since mass units are conservative, the lever rule is fully applicable to wt percent diagrams. A proof of the general validity of the lever rule when conservative units are used is given in appendix 1. Interestingly, a survey of common texts showed that all "rigorous" derivations of the lever rule are given in terms of a conservative unit of quantity. Several texts do ostensibly use gram-formula units, but a careful reading reveals that the result is always couched in gram-component units (for example, Prigogine and Defay, 1954, p. 180; Moore, 1962, p. 128). Of the texts surveyed, only Reisman (1970, p. 145 and p. 222) is complete enough to consider the pitfalls of gram-formula units.

Mineral formulas may be normalized to contain the same number of gram-component units (commonly the same number of atoms, cations, or oxygens) so that the usual mole percent for the normalized formulas is equivalent to gram-component percent. For example, if A, B, and X of figure 5 had all been given with formulas all containing 10 oxides ($A = 9\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$, $B = 4\text{SiO}_2 \cdot 6\text{Al}_2\text{O}_3$, $X = 6\text{SiO}_2 \cdot 4\text{Al}_2\text{O}_3$), then the correct relative proportions would be 60 mole percent solid ($\text{Al}_{12}\text{Si}_4\text{O}_{26}$) and 40 mole percent liquid ($\text{Al}_2\text{Si}_9\text{O}_{21}$) as determined graphically. This procedure, which is advocated by Korzhinskii (1959, p. 34), is cumbersome because it requires mineral formulas to vary with the choice of composition axis endmembers. The procedure is most appropriate for systems of isomorphous minerals, such as feldspars or olivines. We recommend a regular usage of gram-atom units to avoid potential problems.

MEAN ATOMIC THERMODYNAMIC PROPERTIES

One of the most logical applications of gram-atom units is for the normalization of thermochemical data. Since to a first approximation the energies associated with a solid are due to the thermal vibrations of the constituent atoms, energies expressed on a per atom basis should be similar for many minerals. An example would be the well-known law of Dulong and Petit (Moore, 1962, p. 696) which predicts that the heat capacities of solids (at constant volume) will approach a value of $3R$ per gram-atom unit at high temperatures. Figure 6 shows the Gibbs energies of formation from the elements at 298.15K and 10^5 pascals for all the silicates listed in Robie, Hemingway, and Fisher (1978). Taken directly from this compilation, the Gibbs energies are expressed per gram-formula unit of each mineral. Only minerals with the same number of atoms per formula show related values. However, if the same data are normalized on a gram-atom basis (fig. 7), a consistent pattern emerges. Not only does figure 7 emphasize a fundamental similarity among silicate minerals, but it also brings out differences that are not simply due to the number of atoms in the mineral formula.

Also shown in figure 7 are the mean atomic enthalpies of formation of each mineral. Observe that variations in mean atomic Gibbs energies are closely correlated to variations in mean atomic enthalpies. In fact, the difference between $\Delta\hat{G}_{f,298}$ and $\Delta\hat{H}_{f,298}$ is so nearly constant that $\Delta\hat{G}_{f,298}$ may be consistently predicted from $\Delta\hat{H}_{f,298}$ for silicates within 1 percent of the accepted values. This rather surprising observation requires some further discussion.

Constancy of $(\Delta\hat{H}_{f,298} - \Delta\hat{G}_{f,298})$ is of course a constancy of $\Delta\hat{S}_{f,298}$ (mean atomic entropy of formation from the elements). The $\Delta\hat{S}_{f,298}$ for the

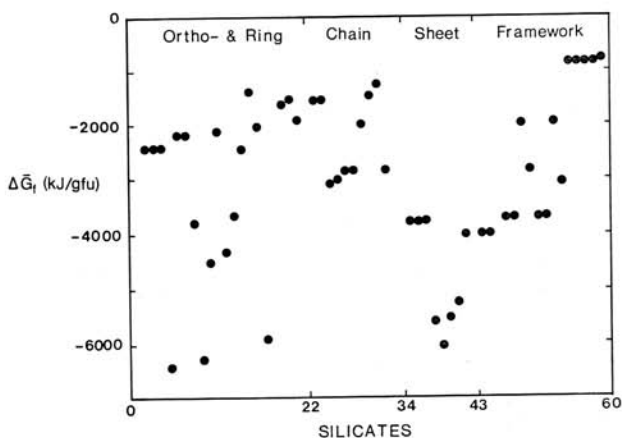


Fig. 6. Molar Gibbs energies of formation for all silicates as listed in Robie, Hemingway, and Fisher (1978). The horizontal axis is simply a means of separating the individual points for comparison. The silicates are shown in the same order that Robie, Hemingway, and Fisher present them. Silica minerals are shown at the extreme right. Several minerals are off scale.

silicates of figures 6 and 7 are shown in figure 8. On the expanded scale of figure 8 relatively small differences among the $\Delta\hat{S}_{f,298}$ for silicates are visible. Although a few minerals (notably fayalite, tephroite, and rhodonite) are out of line, the mean atomic entropies of formation for most silicates are really very similar. This similarity is probably a consequence of two facts: (1) oxygen is a major element in all the silicates, and (2) except for H, F, and Cl, oxygen is the only major element to have a gaseous standard state. The entropy change associated with converting gaseous oxygen to oxygen in a solid silicate apparently overwhelms other entropy differences.

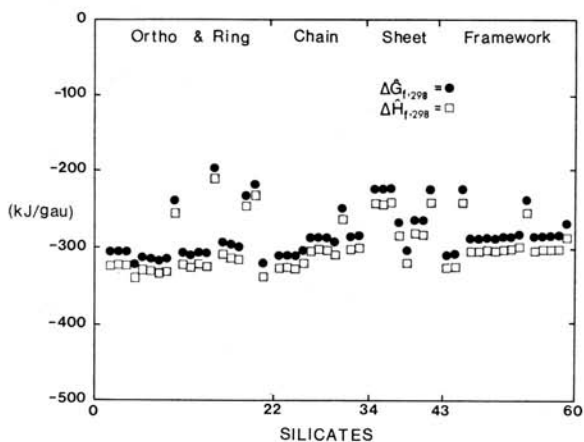


Fig. 7. Mean atomic Gibbs energies of formation from the elements and mean atomic enthalpies of formation from the elements for the silicates of figure 6. Note the consistent separation of the two functions.

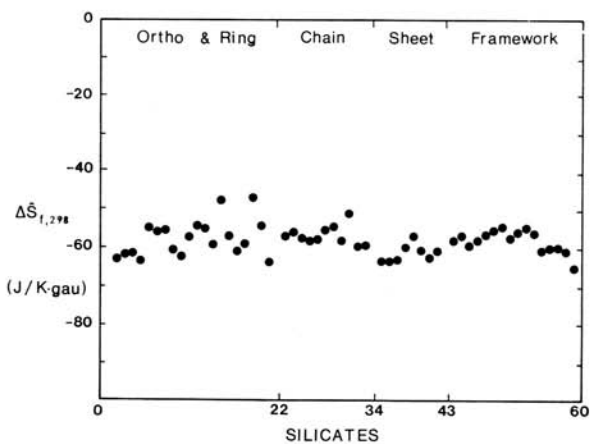


Fig. 8. Mean atomic entropies of formation for the silicates of figure 6. Fayalite, tephroite, and rhodonite are the three least negative points.

We can verify the important role of oxygen in two ways. First, if oxygen does control the $\Delta\dot{S}_{f,298}$, then the consistency of $\Delta\dot{S}_{f,298}$ should apply to minerals other than silicates for which oxygen is a major element. Figure 9 shows the $\Delta\dot{S}_{f,298}$ for all the silicates, multiple oxides, carbonates, sulfates, et cetera listed in Robie, Hemingway, and Fisher (1978). Although the scatter in figure 9 exceeds that of figure 8, the uniformity is still evident. Secondly, the importance of oxygen should lead to consistent entropies when expressed in *gram-oxygen* units. Figure 10 shows $\Delta\dot{S}_{f,298}$ for anhydrous silicates; again, the consistency is striking. Hydrus silicates do not fall on the trend of figure 10, because hydrogen is also gaseous in its standard state. Navrotsky (1974) showed a similar uniformity of $\Delta\dot{S}_f$

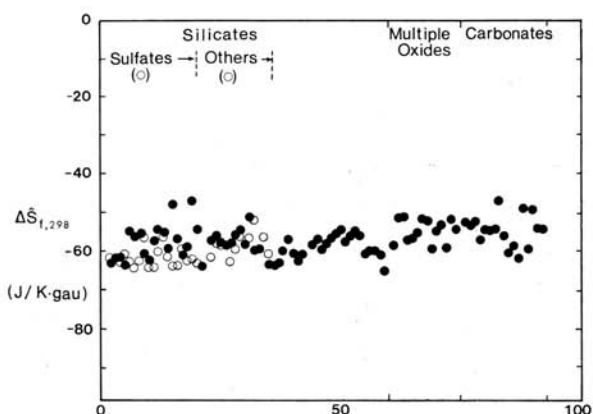


Fig. 9. Mean atomic entropies of formation for the silicates, multiple oxides, carbonates, sulfates, phosphates, molybdates, uranates, and tungstates as listed in Robie, Hemingway, and Fisher (1978).

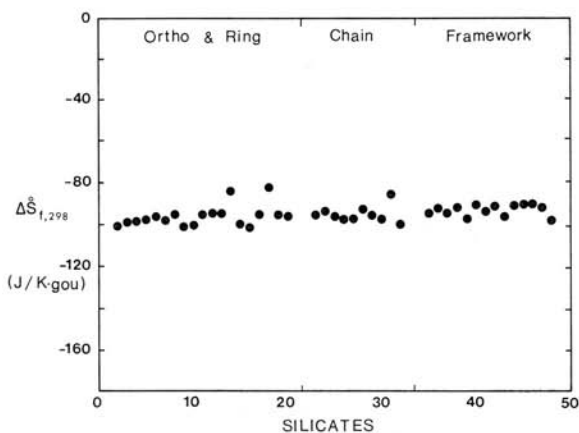


Fig. 10. Entropies of formation per gram-oxygen unit of the anhydrous silicates listed in Robie, Hemingway, and Fisher (1978).

at 1000 K for a large number of binary oxides, although the observed variation is greater for simple oxides due to higher cation to oxygen ratios.

Throughout figures 8 to 10, minerals that have high mean atomic weights seem to have aberrantly high entropies. The predictive value of figures 8 to 10 may be best utilized by either ignoring minerals of high mean atomic weight or by exploiting any entropy-mass relationship that may exist. Figure 11 shows the entropies of figure 9 as a function of mean atomic weight. Although the scatter is significant, there is a clear trend to the data in figure 11 showing a positive correlation between mean atomic weight and entropy. A linear fit to this trend may be used to correct entropy estimates for mass.

A summary of various averaged values for mean atomic entropies of formation is given in table 4. Note that for individual structure groups the standard deviation from the entropy mean is very low. An obvious application of these data would be to obtain Gibbs energies of formation from enthalpy data, where third law entropies are not available. This method compares favorably with other methods available to estimate Gibbs energies from enthalpy data, namely by estimating the third law entropies (see Latimer, 1952; Saxena, 1976; Helgeson and others, 1978). In particular, this procedure has the advantages of simplicity and consistency; it seems to work fairly well for *all* oxygen-based minerals. A similar approach works for chlorine- and fluorine-based minerals (compare Schmalzried and Navrotsky, 1978, p. 152). This procedure is *not* well suited to estimate third law entropies. A 3 percent error in $\Delta\hat{S}_{f,298}$ may lead to a 10 percent error in the standard third law entropy at 298 K, due to the magnitudes of the numbers involved.

CONCLUDING REMARKS

In the preceding paragraphs we have attempted to demonstrate the value of a proper choice of units for petrologic problems. We have found

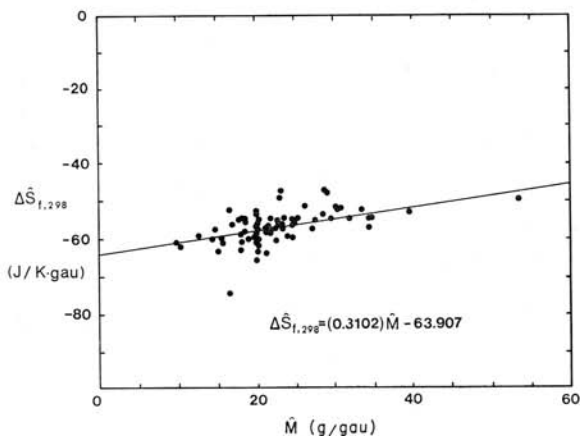


Fig. 11. Mean atomic entropies of formation as a function of mean atomic weight for the silicates, multiple oxides, and carbonates of figure 9. The line and equation are a least squares fit to the data.

TABLE 4
Average values of mean atomic and mean gram-oxygen entropies
of formation from the elements for various mineral groups

Mineral group	$-\Delta\hat{S}_{f,298}$ (J/K-gau)		$\Delta\hat{S}_{f,298}$ (J/K-gou)	
	(inclusive)	(selected)	(anhydrous inclusive)	(anhydrous selected)
Ortho- and ring silicates	57.83(4.77) ^a	58.97(3.39) ^b	96.11(5.13)	97.63(2.47) ^b
Chain silicates	56.97(2.49)	57.55(1.66) ^c	94.99(3.96)	96.07(2.12) ^c
Sheet silicates	61.51(2.31)	62.16(1.52) ^d	—	—
Framework silicates	58.09(2.81)	57.57(2.02) ^e	93.30(2.66)	92.90(2.33) ^e
All silicates	58.27(3.76)	58.74(2.90) ^f	94.97(4.31)	95.77(3.08) ^f
Multiple oxides	54.92(2.99)	—	96.22(5.39)	—
Carbonates	54.85(4.10)	56.19(3.08) ^g	87.99(4.59)	90.32(1.83) ^g
Sulfates	62.19(2.36)	—	93.83(3.15)	—
Other complex oxides	58.46(2.80)	58.99(2.11) ^h	93.28(6.92)	92.08(6.14) ^h
All complex oxides	58.06(4.13)	58.30(2.97) ⁱ	93.90(5.27)	—

^a Data taken from Robie, Hemingway, and Fisher (1978). Values in parentheses are standard deviations from the mean.

^b Excluding fayalite, tephroite.

^c Excluding rhodonite.

^d Excluding fluorophlogopite.

^e Excluding stishovite.

^f See footnotes b, c, d, e.

^g Excluding siderite, rhodochrosite, cerussite.

^h Excluding trisodium uranium oxide.

ⁱ See footnotes b, c, d, e, g, h.

gram-atom units to be especially useful because of their conceptual simplicity, the simple numbers they entail, and their conservative nature. The examples discussed clearly indicate the utility of *conservative* units for any graphical analysis. In addition, the examples show that by an appropriate choice of units, new relationships among old data may emerge.

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APPENDIX I

If the lever rule is to work for the composition axis shown in figure (A1), the following relation must be satisfied:

$$\frac{N_D^X - N_D^A}{N_D^B - N_D^A} \equiv \frac{\frac{n_D^X}{n_C^X + n_D^X} - N_D^A}{N_D^B - N_D^A} = \frac{n_B^X}{n_A^X + n_B^X} \quad (\text{A1})$$

where n_B^X is the number of units of component B in one unit of component X and N_D^X is the composition (gram-unit fraction) of component X in terms of the end mem-

ber components C and D (for example, mass fraction of D in X). To prove the equality (A1) it is necessary to express n_C^X and n_D^X in terms of n_A^X and n_B^X . If the units used are *conservative*, the required stoichiometric relations (eq 1 in text) will be

$$\begin{aligned} 1A &= (1 - N_D^A)C + (N_D^A)D \\ 1B &= (1 - N_D^B)C + (N_D^B)D \end{aligned} \quad (A2)$$

where the sum of the coefficients on either side of these relations is one. It follows from the definition (see text) of the coefficients in eqs (A2) that

$$\begin{aligned} n_C^X &= (1 - N_D^A)n_A^X + (1 - N_D^B)n_B^X \\ n_D^X &= (N_D^A)n_A^X + (N_D^B)n_B^X \end{aligned} \quad (A3)$$

from (A3) it is apparent that

$$(n_C^X + n_D^X) = (n_A^X + n_B^X). \quad (A4)$$

Using (A4) and (A3), (A1) becomes

$$\begin{aligned} \frac{N_D^A n_A^X + N_D^B n_B^X}{(n_A^X + n_B^X)} - N_D^A &= \frac{n_B^X}{(n_A^X + n_B^X)} (N_D^B - N_D^A) \\ N_D^A n_A^X + N_D^B n_B^X - N_D^A n_A^X - N_D^A n_B^X &= N_D^B n_B^X - N_D^A n_B^X \\ (N_D^B - N_D^A)n_B^X &= (N_D^B - N_D^A)n_B^X \end{aligned}$$

confirming the validity of the lever rule for any composition axis based on a conservative unit of quantity. Eqs (A2) do not in general apply to gram-formula units, unless the *formulas* of the minerals are normalized as discussed in the text.

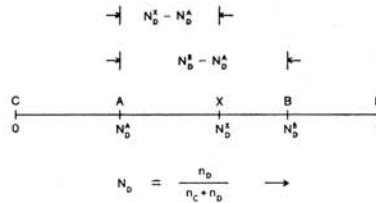


Fig. A1. A composition axis based on the endmember components C and D. The compositions of components A, B, and X are also shown. The unit of quantity is not specified.

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