Theory of immiscibility in mineral systems

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[Taken as read 17 September 1964]

Summary. The theoretical basis for the stability of binary and quasi-binary solutions is discussed with special emphasis on miscibility relations. Solutions of the distribution equations are presented for the case of two and three coexisting regular solutions and this model is used to illustrate the energetics of miscibility relations. The same principles are then extended to give a qualitative interpretation to sequences of mineral assemblages consisting of pyroxenes, amphiboles, micas, and feldspars. A formulation is presented for the *intrinsic stability* of a solution, which depends on the presence or absence of an excess free energy of mixing, and the *extrinsic stability* of a solution, which depends on the standard free energy of the component end members.

ONE of the major objectives in chemical petrology is the deduction of explicit functions relating the variables of state in multicomponental systems. Since the phases which occur in such systems are, with few exceptions, complex mixtures, solution theory has much to contribute to their interpretation. This is especially true in systems in which miscibility gaps occur, and the complex sequences of mineral associations may be interpretable in terms of the energetics of a model.

The equations of thermodynamics alone relate the coexisting phases only implicitly and do not provide a quantitative picture of the system. In order to close this gap we require the equations of state, explicit functions of the chemical potentials in terms of the temperature, pressure, and composition. These functions may be empirically determined as in the case of heat capacities or pressure–volume relations, or they may be based in part on certain theoretical models derived from statistical mechanics. An interesting example of the latter approach is the treatment of silica solubility in water vapor by Wasserburg (1958).

The greatest source of difficulty arises in systems of such complexity that the statistical unit is unknown or poorly defined. Without some knowledge of the atomic structure of a phase it is impossible to construct models of any generality. For such systems the degree of association or polymerization of the simplest units is unknown and consequently neither the ideal configurational entropy nor the excess free energy terms can be deduced. The ultimate example of this situation is to be found in the complex silicate melts in which many different ring, chain, or group polymers may be present simultaneously. A few of these melt systems lend themselves to a multiple solution model approach in which the empirical data are fitted to the most probable association or dissociation schemes.[1] However, such systems may also be treated solely in terms of their macroscopic variables, which do not depend on a detailed solution model. An illustration of this method has recently been presented by the writer (Mueller, 1964).

The situation is somewhat more satisfactory for crystals. The reason for the relative simplicity of the latter is the order imposed by the crystal lattice. In addition the statistical unit is relatively well defined as an atomic or ionic particle in a restricted solution series. The ferromagnesian silicates serve as examples: Although Mg^{2+} and Fe^{2+} interact strongly and to different degrees with the Si–O framework, their interaction with each other is relatively constant throughout the solution series. The result is that the solutions exhibit nearly ideal behaviour (Mueller, 1961).

When the ionic components of a solution series differ markedly in some characteristic such as size or electronic configuration, repulsive forces may arise and a marked tendency to segregate on a microscopic (lattice position) scale may be accompanied by macroscopic exsolution phenomena. Both of these effects are strongly temperature-dependent. Ion pairs that show this behaviour are Ca^{2+}–Mg^{2+} and K^+–Na^+ in the common rock-forming pyroxenes, amphiboles, micas, and feldspars. When several of these solutions coexist it is possible to explain, at least qualitatively, the possible sequence of stably coexisting minerals in terms of the energetics of a non-ideal solution model.

The regular solution model

The simplest solution model that duplicates in a qualitative way many of the characteristics of mineral assemblages is the regular solution first defined by Hildebrand (1929). The basis of this model is the postulate of an ideal entropy of mixing and a partial molar heat of solution that varies as the square of the concentration but is independent of the temperature.[2] Thus the partial molar heat of solution is equal to the corresponding excess free energy.

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[1] See, for example, the recent paper by Knapp and Flood (1961).

[2] A lucid discussion of the statistical basis for the regular solution may be found in the book by Gurney (1949).

The expressions for the relative activities of the components A and B in the binary regular solution are

$$a_A^\alpha = X_A^\alpha \exp\{(1-X_A^\alpha)^2 W^\alpha/RT\} \quad \text{and} \quad a_B^\alpha = (1-X_A^\alpha)\exp\{(X_A^\alpha)^2 W^\alpha/RT\},$$

in which X_A^α refers to the mole fraction $A/(A+B)$ and W^α is the constant factor in the partial molar heat of solution. The general behaviour of the phase α depends on the sign W^α. If this parameter is negative the attraction between the unlike components of the solution is greater than between like components and the solution has an intrinsic stability in excess of that of the ideal solution. Conversely, if W^α is positive the stability of the solution is decreased and if $W^\alpha/RT > 2$ the solution breaks up into two immiscible solutions of different compositions. The result of the latter behaviour is a symmetrical phase diagram in which a plot of the temperature against the composition shows a maximum at $X_A = 0{\cdot}5$.

It is interesting to consider the consequences of the coexistence of two distinct regular solutions, as, for example, α and β with two distinct heat constants W^α and W^β. This is qualitatively similar to certain mineral systems with quasibinary solid solutions. Thus we may have a mixed crystal represented by the formula $(A,B)C$ in which the quasi-binary end members are AC and BC. The second solid solution may be distinguishable from the first by possessing the additional component D. The result is a formula $(A,B)CD$ in which the quasi-binary end members are ACD and BCD. The independently variable components of this system are AC, BC, and D, but both solutions are quasi-binary with respect to A an B. The activities of the β phase are then

$$a_A^\beta = X_A^\beta \exp\{(1-X_A^\beta)^2 W^\beta/RT\} \quad \text{and} \quad a_B^\beta = (1-X_A^\beta)\exp\{(X_A^\beta)^2 W^\beta/RT\}.$$

In both of the above pairs of equations the activities refer to the end members AC, BC, ACD, and BCD. Consequently no simple transfer reaction connects the phases $(A,B)C$ and $(A,B)CD$. The proper reaction to consider is the exchange reaction $ACD+BC \rightleftharpoons BCD+AC$. If we combine the four activities $a_A^\alpha, a_B^\alpha, a_A^\beta, a_B^\beta$ in the conventional way we obtain the expression for the equilibrium constant:

$$K_a = \frac{(1-X_A^\beta)X_A^\alpha \exp\{(1-2X_A^\alpha)W^\alpha/RT\}}{(1-X_A^\alpha)X_A^\beta \exp\{(1-2X_A^\beta)W^\beta/RT\}}.$$

Solutions for this transcendental equation may easily be obtained by graphical means or by use of an electronic computer.

In order to illustrate the behaviour of this equation in the range of unmixing we assign the values $W^\alpha = 3072$ calories, $W^\beta = 2875$ calories. From the formula $W/RT_C = 2$ these values correspond to the critical temperatures $T_C^\alpha = 500°$ C and $T_C^\beta = 450°$ C. To evaluate the effect of the equilibrium constant we may assume that to a first approximation the standard free energy of the reaction $ACD+BC \rightleftharpoons BCD+AC$ is a constant and equal to 300 calories. Consequently $\ln K_a$ is an inverse function of the temperature, and we obtain

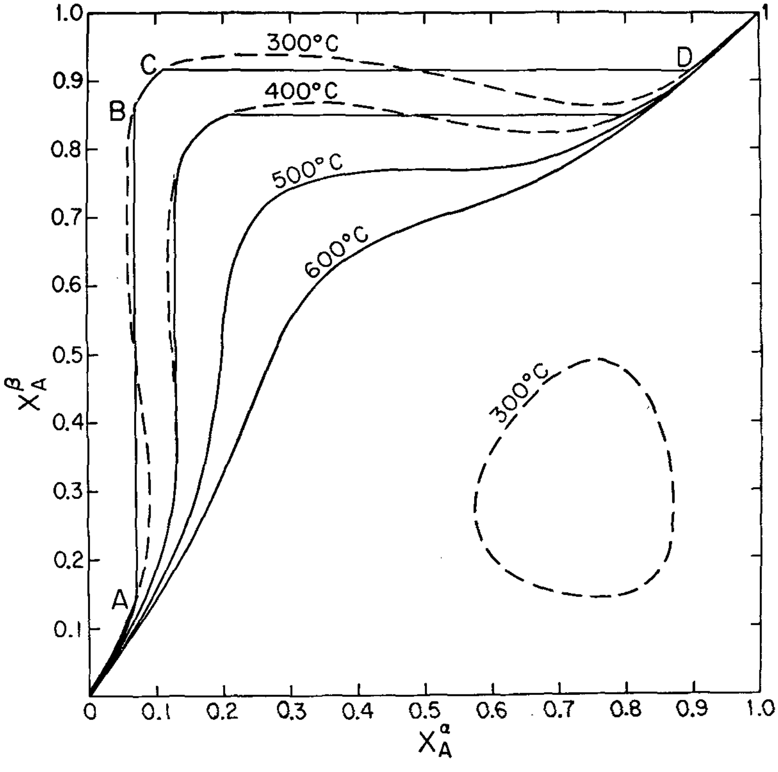

Fig. 1. Theoretical distribution diagram for coexisting regular solutions. Dashed portions of curves indicate metastable and unstable compositions in which immiscibility occurs. Immiscibility gaps are shown as straight full lines.

$$\exp(-300/RT) = \frac{(1-X_A^\beta)X_A^\alpha \exp\{(1-2X_A^\alpha)3072/RT\}}{(1-X_A^\alpha)X_A^\beta \exp\{(1-2X_A^\beta)2875/RT\}}.$$

Fig. 1 is a graph of this equation for various temperatures over the entire composition range. The full curves represent stable compositional ranges of the coexisting solutions and the dashed curves metastable and unstable ranges. At 600° C there are two coexisting solutions α and β over the entire range. At 500° C the α solution has attained its critical point as shown by the horizontal inflexion. At 400° C both α and β have split into two solutions and the miscibility gap is largest for the α solutions. The final curve for 300° C shows a closed, isolated segment for this temperature in the lower right-hand region. This segment illustrates the complexities that may arise even in these comparatively simple functions. The metastable and unstable segments, which are direct continuations of the stable portions of the curves, are of course easily predictable from the corresponding segments in the activity curve. However, the closed region is not so readily apparent from the initial design of the model.

Interpretation of sequences of mineral assemblages

Fig. 1 represents univariant and invariant states of an isobaric-isothermal system. The thermodynamic characteristics of continuous distribution curves for such systems have been previously treated (Mueller, 1961). In the more general system under discussion here a sequence of 'mineral' assemblages may be constructed by varying the composition along the path 0–*ABCD*–1 as shown in fig. 1. An alternative and somewhat more familiar means of depicting these relations for a given temperature is shown in fig. 2, which shows the relation for 300° C. It should be kept in mind that the slopes of the tie-lines in fig. 2 are highly significant since they relate directly to the analytic expression and the energetics of the system. These figures show that three two-phase and two three-phase fields are traversed when the species B is exchanged for the species A.

Although it would not be expected that many mineral systems would obey the relatively simple solution models represented by figs. 1 and 2, it might well be expected that *qualitatively* similar relations would be fairly common. It is implied in the geometry of the figures that two different types of curves or crystallization paths are possible, depending on whether the α or β phase develops a miscibility gap first. These two alternatives are depicted in a qualitative way in fig. 3 as the paths 0–*ABCD*–1 and 0–*A′B′C′D′*–1. Such diagrams may in principle be used to interpret a variety of mineral assemblages in terms of the sequence of coexisting pairs and trios of minerals that appear. This may best be illustrated by reference to specific systems. We may begin with the system $CaSiO_3$–$MgSiO_3$–SiO_3H_2. The members of this system that regularly appear in metamorphic rocks are diopside, enstatite, tremolite,

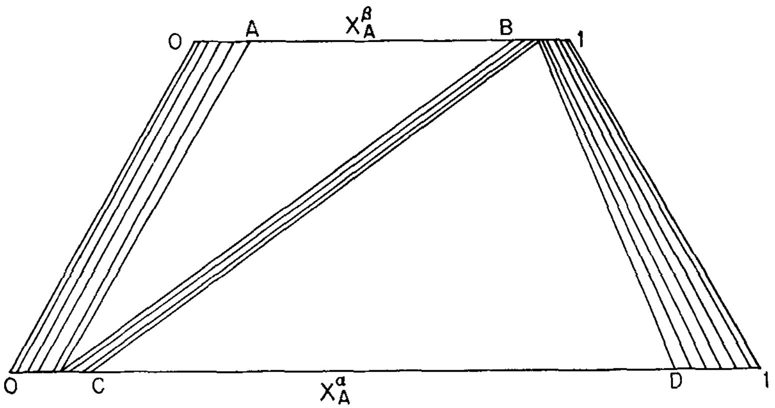

FIG. 2. A triangular plot of the 300° C data of fig. 1.

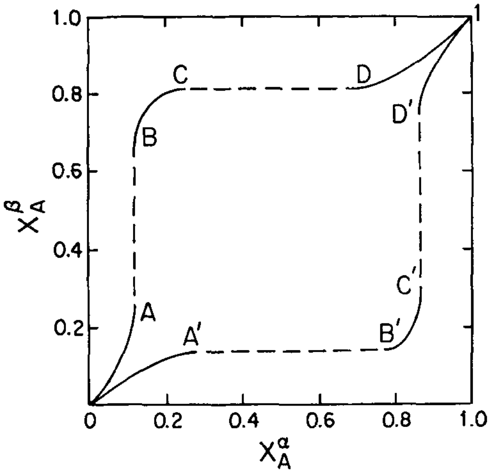

FIG. 3. Qualitative illustration of alternative sequences of coexisting solution based on immiscibility model.

and cummingtonite (or anthophyllite). In these minerals the calcium and magnesium components form very non-ideal solutions and miscibility gaps occur in both amphiboles and pyroxenes. If, therefore, we represent the composition of the pyroxenes between $CaMgSi_2O_6$ and $Mg_2Si_2O_6$ as the abscissa and the composition of the amphiboles between

$Ca_2Mg_5Si_8O_{22}(OH)_2$ and $Mg_7Si_8O_{22}(OH)_2$ as the ordinate we can distinguish between the two possible sequences of coexisting mineral pairs and trios:

0–*A*, tremolite–diopside; *A*–*B*, tremolite–diopside–kupfferite;[1] *B*–*C*, diopside–kupfferite; *C*–*D*, diopside–kupfferite–enstatite; *D*–1, kupfferite–enstatite; excluded, tremolite–enstatite.

Or 0–*A'*, tremolite–diopside; *A'*–*B'*, tremolite–diopside–enstatite; *B'*–*C'*, tremolite–enstatite; *C'*–*D'*, tremolite–enstatite–kupfferite; *D'*–1, enstatite–kupfferite; excluded, diopside–kupfferite.

We see that one pair of minerals is excluded in each case, a fact that may be used to deduce the correct assemblage. In nature other elements are usually present so that the solutions are more complex. One of the commonest additional species is Fe^{2+}, which behaves similarly to Mg^{2+} in relation to Ca^{2+}. It is in fact in the metamorphic iron formations, in which Fe^{2+} is abundant, that the above sequence is best developed. Examples of these iron formation assemblages have been presented by Mueller (1960) and by Kranck (1961). In these assemblages the pair actinolite–orthopyroxene (corresponding to tremolite–enstatite) does not occur,[2] but the pair Ca-pyroxene–cummingtonite is of wide occurrence. These relations hint that the first of the above sequences is probably the correct one. Of course certain members of a pair or trio might at times be excluded for other reasons. For example the partial pressure of water might be too high or too low. Thus tremolite and kupfferite[3] might occur without diopside.

We must also remember that these simple deduced sequences may be upset by the presence of such ions as Al^{3+}, which have marked effects on the energetic properties of minerals (Kretz, 1960). Thus Al^{3+} might stabilize an otherwise incompatible association. For example, aluminous hornblende and orthopyroxene are frequently associated in granulite facies rocks (Ramberg, 1949).

A further example is provided by the sequence of coexisting feldspar and mica in the system $KAlSi_3O_8$–$NaAlSi_3O_8$–$Al_2O_4H_2$. This system has been investigated experimentally by Eugster and Yoder (1954) and studied in the field by Banno (1960). The sequence of coexisting micas and feldspars obtained with a change in the ratio K : (K + Na) appears to be entirely analogous to the case of the pyroxenes and amphiboles just

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[1] i.e. kupfferite (of Allen and Clement) = magnesio-anthophyllite [Ed.].

[2] Kranck reports one minor occurrence of a 'light green amphibole' with hypersthene, but the composition of this amphibole is not given.

[3] Pure kupfferite has never been found and is probably unstable in the extrinsic sense.

discussed. For example, the assemblage Na-rich feldspar and K-rich mica (muscovite) is common, but the coexistence of Na-rich mica (paragonite) with K-rich feldspar seems excluded.

Intrinsic and extrinsic stability relations

The stability relations of solid solutions may be divided into two types: *intrinsic* and *extrinsic*. The immiscibility effects just discussed are of the intrinsic type since the internal stability or instability of the solution *per se* governs whether or not a new phase appears. Thus solutions at a given pressure and temperature are stable or unstable entirely by virtue of their excess free energies of solution. It is obvious that ideal solutions are always intrinsically stable since the excess free energy is zero, and the free energy of mixing has a fixed negative value at a given temperature and concentration. Therefore ideal solutions can only be extrinsically unstable since their instability must be related to some factor other than the inherent solution properties.

Extrinsic instability arises from the instability of the pure components or end members of the solution relative to certain reaction products. An example of this type of instability occurs in the system Mg_2SiO_4–Fe_2SiO_4–SiO_2. There is considerable evidence that both Mg–Fe pyroxenes and olivines form nearly ideal solutions (Sahama and Torgeson, 1949; Mueller, 1961). Yet at liquidus temperatures Bowen and Schairer (1935) found that pyroxenes of more than 55 mol. % ferrosilite could not exist. At lower temperatures a higher ferrosilite content ($\approx$ 84 %) becomes stable but pure ferrosilite has never been synthesized. The upper limit to the quantity of iron a pyroxene may contain is therefore uncertain, but it is possible that pure ferrosilite may be stable under a limited range of conditions. This type of instability may be illustrated by the reaction ferrosilite $\rightarrow$ fayalite + silica, which governs the relations in some situations. Although inadequate thermal data exist for ferrosilite to compute ΔG_b^0, the standard free energy change for this reaction, a negative value is indicated by the distribution of Fe^{2+} and Mg^{2+} between olivine and pyroxene (Ramberg and De Vore, 1951). If both minerals are ideal solutions we obtain $\exp(-\Delta G_b^0/2RT) = X_{Fe}^{ol}/X_{Fe}^{px}$, in which the X_{Fe}^{ol} and X_{Fe}^{px} refer to the ratio $Fe^{2+}/(Fe^{2+}+Mg^{2+})$ in the olivine and pyroxene respectively. Since $(X_{Fe}^{ol}/X_{Fe}^{px}) > 1$, ΔG_b^0 must be negative. Iron-rich solid solutions of pyroxene are thus unstable because of the instability of ferrosilite relative to fayalite and quartz.

Some ferromagnesian solid solutions appear to have an excess intrinsic stability over the ideal model. Thus cummingtonite was found to have a negative excess free energy of mixing (Mueller, 1961).

The stability relations of complex mineral assemblages are frequently depicted as in fig. 2, in which two-phase fields alternate with three-phase fields. When such diagrams refer to the fraction $Mg^{2+}/(Mg^{2+}+Fe^{2+})$ they usually depict complex extrinsic stability relations. When, on the other hand, a diagram refers to the fraction $Ca^{2+}/(Ca^{2+}+Mg^{2+})$ or other fractions of unlike ions the relations depicted may involve both extrinsic and intrinsic relations. Diagrams of such complexity have little predictive value since the extrinsic stability relations cannot be anticipated with any degree of confidence in the absence of thermochemical data.

Acknowledgements. Some of the computations used in this paper were made while the writer was at the University of California at San Diego. The use of computer facilities is gratefully acknowledged.

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